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The University of Osaka

Doctoral Dissertation

Effects of Heat Treatment on the Electrochemical
Performance of Electrodes for Vanadium Redox
Flow Batteries

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December 2025

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The University of Osaka

Contents

Chapter 1 Introduction	1
1.1 Background and research motivation	1
1.2 Cell performance and overpotentials.....	3
1.3 Electrode modification strategies for VRFBs	5
1.3.1 Physical activation and heat treatment	6
1.3.2 Chemical and electrochemical functionalization.....	7
1.3.3 Deposition of catalytic nanoparticles	8
1.3.4 Non-metallic heteroatom doping.....	10
1.3.5 Summary of electrode modification strategies	11
1.4 Research motivation, framework, and contributions.....	13
1.4.1 Controversies and knowledge gaps	13
1.4.2 Research framework.....	14
1.4.3 Objectives and main contributions	16
1.5 Thesis structure	18
<i>References</i>	19
Chapter 2 Methods	29
2.1 Materials.....	29
2.2 Electrode preparation	31
2.3 Symmetric cell configuration	32
2.4 Physicochemical characterization	34
2.4.1 Scanning electron microscopy and energy-dispersive X-ray spectroscopy	34
2.4.2 Raman spectroscopy.....	34
2.4.3 X-ray photoelectron spectroscopy.....	35
2.4.4 Contact angle.....	35
2.4.5 Porosity	36
2.5 Electrochemical measurements	36

2.5.1 Polarization (I-V) curves	36
2.5.2 Electrochemical impedance spectroscopy	36
2.5.3 Overpotential decomposition	38
2.5.4 Tafel analysis.....	39
2.5.5 Electrochemical surface area and standard rate constant	39
2.5.6 Estimation of effective ionic resistance.....	42
2.6 Normalization and parameter definitions	43
2.6.1 Charge transfer normalization.....	44
2.6.2 Mass transport characterization.....	44
2.6.3 Ohmic correction.....	46
2.6.4 Normalization summary	47
<i>References</i>	50
Chapter 3 Heat Treatment Effects on Carbon Electrodes	52
3.1 Introduction	52
3.2 Morphology.....	53
3.3 Surface chemistry.....	55
3.3.1 Raman spectroscopy.....	55
3.3.2 X-ray photoelectron spectroscopy.....	56
3.4 Wettability and porosity	59
3.4.1 Wettability.....	60
3.4.2 Porosity	61
3.5 Summary	62
<i>References</i>	65
Chapter 4 Electrode Heat Treatment in Symmetric Cells: V^{2+}/V^{3+} Half Reaction.....	67
4.1 Introduction.....	67
4.2 Overall electrochemical performance	68
4.3 Decomposition of overpotentials	72

4.3.1 Charge transfer overpotential	74
4.3.2 Mass transport overpotential	81
4.3.3 Ohmic overpotential	83
4.3.4 Overall overpotential decomposition	85
4.4 Conclusions	87
<i>References</i>	89
Chapter 5 Electrode Heat Treatment in Symmetric Cells: $\text{VO}^{2+}/\text{VO}_2^+$ Half Reaction.....	92
5.1 Introduction	92
5.2 Precipitation overpotential	93
5.2.1 Overall polarization curves	93
5.2.2 Nyquist analysis under DC bias	95
5.2.3 EIS limitation under precipitation	96
5.2.4 Quantification of precipitation overpotential	98
5.2.5 Mechanistic clarification	99
5.2.6 Morphological and spectroscopic verification	101
5.3 Decomposition of overpotentials	105
5.3.1 Charge transfer overpotential	105
5.3.2 Mass transport overpotential	109
5.3.3 Ohmic overpotential	111
5.3.4 Overall cell performance	112
5.4 Conclusions	114
<i>References</i>	116
Chapter 6 Comparison Between the $\text{V}^{2+}/\text{V}^{3+}$ and $\text{VO}^{2+}/\text{VO}_2^+$ Symmetric Cells	120
6.1 Introduction	120
6.2 Charge transfer intrinsic parameters	120
6.3 Mass transport limitation.....	124
6.4 Ohmic resistance	126

6.5 Unified dimensionless overpotential comparison	127
6.6 Summary	130
<i>References</i>	132
Chapter 7 Conclusions & Perspectives	133
7.1 Conclusions	133
7.2 Perspectives	137
List of publications	140
Acknowledgements	142

Chapter 1

Introduction

1.1 Background and research motivation

Fossil fuel reserves have been declining, and concern about greenhouse gas emissions is increasing, pushing a global shift to low-carbon energy. In recent years, the share of renewable energy, especially wind and solar power, has increased rapidly in the electricity supply of many countries [1]. Unlike conventional fossil fuel-based power generation, wind and solar energy are inherently variable and weather dependent, resulting in significant fluctuations in power output on daily, seasonal, and annual timescales [2]. These fluctuations result in considerable challenges for grid balancing and reliable electricity supply because the penetration of renewable energy continues to rise.

To address these issues, the deployment of large-scale and reliable energy storage technologies has become essential. Energy storage systems can smooth power fluctuations, absorb excessive renewable generation, and release electricity during periods of low output, thereby supporting stable grid operation and enabling higher renewable integration. Because of these needs, annual installations of energy storage systems are expected to exceed 400 GWh by 2030, with a compound annual growth rate above 20% [3]. As a result, the development and application of advanced stationary energy storage have become central to the transition toward sustainable power systems.

Among the available storage technologies, vanadium redox flow batteries (VRFBs) have been widely studied and used for stationary energy storage systems, particularly in applications requiring long-duration and high safety. VRFBs are a class of electrochemical energy storage devices in which energy is stored in the oxidation states of vanadium ions dissolved in sulfuric acid solutions. The system includes two external electrolyte tanks, a battery stack containing ion-exchange membranes and porous carbon electrodes, and a pumping and circulation subsystem.

During discharging, vanadium ions undergo reversible redox reactions at the electrodes:

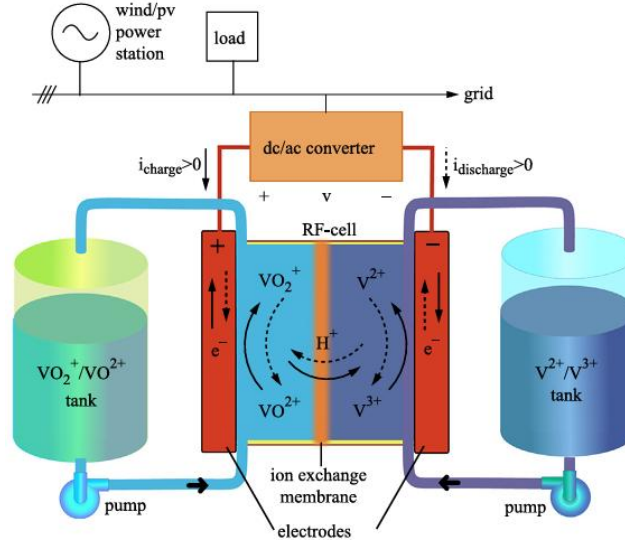
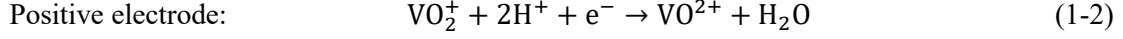
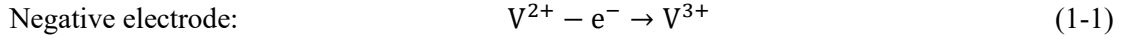


Fig. 1-1 Diagram of a vanadium redox flow battery system [4]

The use of vanadium as the only redox-active element in both half cells largely eliminates cross-contamination and capacity fades due to crossover of active species, which is a unique advantage of VRFBs compared to other flow battery chemistries [5]. Moreover, the fundamental structure of VRFBs allows independent scaling of power (determined by the battery stack) and energy (determined by the electrolyte tank), providing flexibility for grid-scale operation [6]. The use of aqueous electrolytes avoids fire risks, and VRFBs can achieve long service lifetimes with minimal capacity loss over thousands of cycles [7,8]. Large-scale commercial VRFB projects, including the 200 MW/800 MWh plant in Dalian, China, and several megawatt-scale installations in Japan, demonstrate the technology's practical feasibility [9].

Despite these advantages, there are still important technical and economic challenges. The cost of vanadium electrolytes remains high and accounts for about 40% of the total capital investment, and fluctuations in raw material prices can significantly affect the levelized cost of

storage [10]. Furthermore, the achievable operational power density is limited by charge transfer, mass transport, and ohmic overpotentials, which require large electrode areas and result in higher stack costs [11]. Improving electrode and stack performance is therefore essential to lower cost further and large-scale application of VRFBs.

Compared to other stationary storage technologies such as lithium-ion, sodium-sulfur, and lead-acid batteries, VRFBs offer advantages in terms of cycle life, safety, and deep discharge tolerance [12,13]. For grid-level, long-duration applications (> 4 h), these features are particularly valuable. However, further development is required to address issues such as electrolyte stability, vanadium ion crossover, system efficiency, and overall complexity [14]. In addition, government policies in regions such as the United States and the European Union are increasingly supporting the demonstration and deployment of long-duration energy storage, providing opportunities for further advancement of VRFB technology [15].

Therefore, continued research into the performance gains of VRFBs, including power density, charge transfer, mass transport, long-term stability and other key factors are essential for supporting the transition to renewable energy systems.

1.2 Cell performance and overpotentials

As discussed in Section 1.1, one of the major technical and economic challenges facing VRFBs is their relatively low power density compared to other battery systems. Power density, which describes the amount of electrical power produced per unit area of the battery stack, is a key factor determining the size, material consumption, and overall cost of a flow battery system. In practical applications, insufficient power density leads to the need for larger electrode areas and more extensive stack hardware to achieve the desired output, which significantly increases both the capital cost and the space needed for the installation [16].

From a technical and economic perspective, the cost structure of a commercial VRFB system is highly sensitive to the power density of the stack. Studies have shown that the stack and related hardware, including electrodes, bipolar plates, current collectors, and flow frames, can

account for more than 30% of the total system cost [17]. When the operational current density is low, more electrodes and hardware are required to meet target power ratings, resulting in a proportional increase in materials and assembly costs.

The fundamental reason for the power density limitation in VRFBs is the presence of multiple overpotentials during operation, each dominating in a different current density range. At low current densities, activation overpotential, which is charge transfer overpotential, arising from slow kinetics of the V^{2+}/V^{3+} and VO^{2+}/VO_2^+ redox reactions at the electrode-electrolyte interface, is the primary contributor. As current density increases, ohmic losses, determined mainly by the resistance of the membrane, electrodes, and cell connections, become the dominant limitation in the intermediate area. At high current densities, mass transport overpotential becomes critical, as the supply of reactants and removal of products in the porous electrodes and electrolyte channels becomes insufficient, leading to concentration gradients and reactant consumption near the electrode surfaces [18].

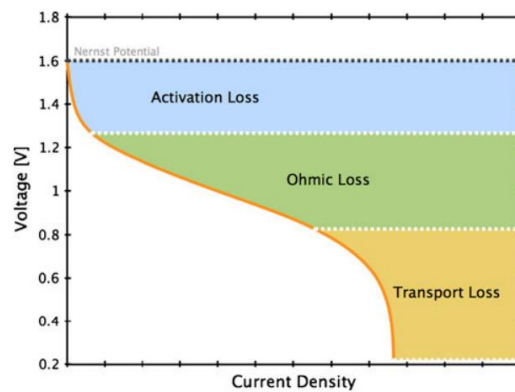


Fig. 1-2 Three types of overpotentials in VRFB systems [19]

These three types of overpotential together reduce the effective cell voltage and restrict the maximum current. Therefore, optimizing both electrode materials and cell design to minimize each type of overpotential is essential for improving VRFB power density and efficiency. Among these, charge transfer and mass transport overpotentials are most strongly affected by the properties of the electrodes and the design of the cell. In particular, pristine carbon felts or papers,

which are widely used as VRFB electrodes, often exhibit limited electrochemical active surface area, poor wettability, and low catalytic activity, resulting in high overpotentials and restricted power output [20–22]. As a result, improving electrode materials and structures to reduce charge transfer and mass transport overpotentials has become a primary strategy for enhancing VRFB power density and lowering system cost.

Therefore, a comprehensive understanding of the mechanisms behind power density limitation, as well as the development of effective approaches to reduce overpotentials, is essential for the commercial viability and large-scale deployment of VRFB technology.

1.3 Electrode modification strategies for VRFBs

Commercial carbon felts and papers are the most common electrodes in VRFBs. They are produced from polyacrylonitrile (PAN) or rayon-based fibers by carbonization, forming an interconnected fiber network with high porosity and adequate permeability for electrolyte circulation [23]. However, the native fiber surfaces are relatively smooth and graphitized, which limits the electrochemical surface area (ECSA) and slows interfacial charge transfer for both the V^{2+}/V^{3+} and VO^{2+}/VO_2^+ couples [24]. In kinetic terms, pristine electrodes usually exhibit a low standard rate constant k_0 , as determined from Tafel analysis, electrochemical impedance spectroscopy (EIS), or carefully interpreted cyclic voltammetry (CV), and a lower k_0 is directly associated with a higher charge transfer overpotential at a given current density [25]. Poor wettability in acidic vanadium electrolytes can further reduce the accessible surface area during initial operation, so the effective surface area for reactions may be very small [26].

In addition, the pore structure of pristine felts is not necessarily optimized for both electronic conduction and convective-diffusive transport. Moderate compression can improve interfacial contact and reduce ohmic losses, but excessive compression narrows through-plane pathways and may increase mass transport polarization at higher current densities [27]. These trade-offs motivate modification strategies that adjust surface chemistry and pore networks. Thus, it is important to enlarge ECSA, improve wetting, and reduce charge transfer and mass transport

overpotentials while keeping ohmic resistance acceptable.

1.3.1 Physical activation and heat treatment

Heat activation is a widely adopted physical method to improve the surface activity and wettability of carbon felts and papers used in VRFBs. The treatment typically involves heating in the air, oxygen, or other oxidative atmospheres at temperatures between 300 °C and 500 °C for several hours [28]. Oxidative heat treatment introduces oxygen functional groups (e.g., -OH, -COOH, -C=O) and increases surface roughness by roughening fiber surface, thereby enhancing hydrophilicity and the density of electrochemically active sites [29]. These changes can reduce the charge transfer resistance and increase the standard rate constant k_0 , especially for the V^{2+}/V^{3+} couple.

The effects of heat activation are not identical for the two half-reactions. For the V^{2+}/V^{3+} couple (negative electrolyte side), it was reported that a significant increase in k_0 occurred after controlled activation, often by one order of magnitude or more, leading to faster kinetics and lower charge transfer overpotentials [30]. For the VO^{2+}/VO_2^+ couple (positive electrolyte side), however, the literature is mixed: some works found moderate improvements in k_0 , while others observed little benefit or even deterioration, particularly when certain oxygen functional groups acted as inhibitors [31–33]. This is commonly attributed to adsorption behavior and interfacial electron transfer on oxidized carbon surfaces [34,35].

Heat activation also influences mass transport indirectly. Increased wettability allows deeper electrolyte penetration into the porous carbon structure, making more of the internal surface area electrochemically accessible. However, excessive oxidation can cause fiber embrittlement, loss of electrical conductivity, and collapse of the porous network, increasing ohmic resistance and potentially worsening performance at high current densities [36]. Therefore, an optimal balance between surface oxidation, structural integrity, and electronic conductivity is required.

Overall, as the most widely used electrode modification method, heat treatment still needs

further optimization of experimental conditions to obtain the best performance. In practice, mild heat treatment at 400-500 °C in air or oxygen has been reported to achieve a good compromise between raising k_0 , enhancing wettability, and maintaining conductivity [36].

1.3.2 Chemical and electrochemical functionalization

Chemical and electrochemical methods provide another effective way to improve the surface activity and wettability of carbon electrodes in VRFBs. Compared with purely physical activation, these approaches allow finer control of surface chemistry, especially introducing polar groups that promote hydrophilicity and enhance charge transfer kinetics [37].

A common strategy is acidic oxidation using nitric acid, sulfuric acid, or mixed oxidants. Such treatments generate oxygen functional groups (e.g., -OH, -C=O, -COOH) and form defect sites on the basal plane, showing that these modifications increase the electrocatalytic activity and decrease charge transfer resistance [38]. For example, electrodes treated in concentrated nitric acid vapor showed up to a 100% increase in discharge capacity compared with pristine felts, indicating an efficient electrocatalysis towards the V^{2+}/V^{3+} and VO^{2+}/VO_2^+ redox pairs [39]. However, strong acid treatments may cause over-oxidation, leading to pore collapse, reduced conductivity, and even structural fragility [40].

Plasma treatment is another widely studied method. Oxygen, nitrogen, and argon plasmas can modify the surface layer within minutes, introducing polar functional groups while avoiding uneven distribution [41]. It has been proven that oxygen plasma can significantly increase the formation of oxygen functional groups and cell energy efficiency [42]. Nitrogen plasma can also introduce nitrogen functional groups, resulting in defects on the carbon electrode and increasing the reaction edge sites, which improves electrochemical performance [43]. However, the durability of the induced surface functionalities in concentrated sulfuric acid remains uncertain, and their stability should be tested in long-term cycling [44].

Electrochemical activation, carried out by applying potential sweeps or holds directly in vanadium electrolytes, provides a simple in-situ method. This process not only increases surface

activity but also pretreats the electrode under the practical potential and electrolyte conditions. For example, CV has been verified to modify the surface of carbon electrodes: the kinetics of V^{2+}/V^{3+} were enhanced by anodic and inhibited by cathodic treatment; in contrast, the kinetics of VO^{2+}/VO_2^+ were inhibited by anodic, and enhanced by cathodic treatment [45,46]. It is shown that outcomes are sensitive to protocol parameters such as potential window and scan rate, and reproducibility can be limited if conditions are not standardized.

Overall, chemical and electrochemical functionalization reliably improve wettability and increase k_0 , especially at low and intermediate current densities where activation losses dominate. While improved wettability enhances utilization of inner pores and can mitigate mass transport limitations, any surface damage or internal structural collapse of the carbon electrode caused by overly aggressive treatments may offset these gains. Therefore, balancing treatment severity against structural stability is critical for practical application.

1.3.3 Deposition of catalytic nanoparticles

Deposition of catalytic nanoparticles has been widely investigated to further reduce the charge transfer resistance of VRFB electrodes. The intrinsic catalytic activity of pristine carbon is limited, so attaching nanoparticles can provide additional electroactive sites, enhance charge transfer, and increase the ECSA [47].

Noble metals such as Pt, Ir, and Ag demonstrate excellent electrocatalytic activity toward vanadium redox couples. For instance, Pt-decorated graphite felt was reported to improve cell energy efficiency by 11.58% due to faster electrode kinetics [48]. Ir-modified carbon felt also increased VO^{2+}/VO_2^+ activity and reduced the overpotential required for the reaction. The cell resistance decreased by about 25% compared with unmodified felt [49]. Similarly, Ag nanoparticles uniformly deposited on carbon fibers significantly reduced the activation energy of the V^{2+}/V^{3+} redox reaction, thereby accelerating the reaction kinetics and reducing the charge transfer resistance by nearly 300-fold [50]. However, the high cost and scarcity of noble metals limit their large-scale use, so this method is mainly used in fundamental studies or in hybrid

designs.

Non-noble catalysts such as Bi, Cu, and Prussian Blue (PB) have been investigated as low cost alternatives for VRFB electrodes. Bi nanoparticles significantly improved the electrochemical performance by enhancing the sluggish V^{2+}/V^{3+} redox reaction kinetics. Compared with cells without Bi, the energy efficiency at high current density (150 mA/cm^2) increased by 11% due to faster charge transfer [51]. The copper nanoparticle-deposited graphite felt electrode reached an energy efficiency of 80.1% at a current density of 300 mA/cm^2 , which was about 17.8% higher than cells without the catalyst [52]. Moreover, the PB/carbon felt electrode exhibited excellent electrochemical activity for the VO^{2+}/VO_2^+ redox couple in vanadium batteries, achieving an energy efficiency of 88% at a current density of 100 mA/cm^2 [53]. These results show that non-noble catalysts can offer notable kinetic enhancement at lower cost, though further work is needed to maintain stability during long-term cycling.

Transition metal oxides have been widely studied due to their low cost, multiple oxidation states, and rich surface redox active sites, with TiO_2 , WO_3 , Mn_3O_4 , and CeO_2 being the most representative. Adding 20 wt% TiO_2 to the carbon felt electrode increased the ECSA and specific capacitance, resulting in the energy efficiency increase from 56.4% of the original carbon felt cell to 65.4% at 200 mA/cm^2 [54]. WO_3 has good corrosion resistance in acidic media. After being coated on the surface of carbon paper, its electrochemical activity was improved, and the energy efficiency reached 80.5% at 50 mA/cm^2 [55]. Also, compared with commercial carbon felt electrodes, the modified carbon electrode doped by 20% Mn_3O_4 increased energy efficiency from 70% to 81%, attributed to the higher oxygen species content and the improved electronic conductivity [56]. Moreover, by modifying the carbon felt surface with CeO_2 , the energy efficiency of the carbon felt modified with 0.2 wt% CeO_2 was 10.8% higher than original carbon felt at 200 mA/cm^2 , because CeO_2 improved the electrochemical activity and hydrophilicity of vanadium ions [57]. These results show transition metal oxides are one of the candidates for VRFBs due to their low cost and good catalytic performance, but their relatively low intrinsic

conductivity and instability in acidic environments usually require careful design.

Overall, deposition of catalytic nanoparticles can effectively enhance kinetics for both half-cell reactions, particularly by raising the standard rate constant k_0 and ECSA to lower charge transfer overpotential. However, the high cost and scarcity of noble metal catalysts, the long-term stability of non-noble metal catalysts, and the degradation of transition metal oxide catalysts in acidic environments remain major challenges to future commercialization [58].

1.3.4 Non-metallic heteroatom doping

Heteroatom doping has become an important strategy to enhance the electrochemical activity of carbon electrodes in VRFBs. Among the possible dopants, nitrogen has been most widely studied due to its multiple bonding configurations in carbon frameworks and its significant influence on vanadium redox kinetics. In addition to nitrogen, co-doping with other elements such as phosphorus or sulfur has also been explored, since introducing multiple heteroatoms can synergistically modulate the electronic structure, increase defect density, and improve surface polarity. These modifications not only enhance wettability, conductivity, and electrolyte infiltration but also create additional active sites for vanadium redox reactions, thereby lowering charge transfer resistance [59]. Compared with nanoparticle deposition, heteroatom doping is attractive due to its low cost, scalability, and the absence of issues related to particle detachment.

Nitrogen doping is the most widely studied approach among heteroatom modifications. N atoms can be incorporated into carbon frameworks in different configurations, such as pyridinic-N, pyrrolic-N, and graphitic-N (quaternary-N). When the relative content of the quaternary-N in the modified nitrogen-doped carbon electrode was the highest, it has been reported to exhibit higher catalytic activity for $\text{VO}^{2+}/\text{VO}_2^+$, because quaternary-N is more stable in acidic environment and promotes the adsorption process of $\text{VO}^{2+}/\text{VO}_2^+$ on the active sites [60]. Also, it was claimed that the enhancement of $\text{V}^{2+}/\text{V}^{3+}$ kinetics by nitrogen-doped carbon electrodes was attributed to the enhanced adsorption of vanadium on pyridinic-N, while the promoted $\text{VO}^{2+}/\text{VO}_2^+$ kinetics was attributed to the significantly reduced activation energy barrier

by doping N atoms [61]. Moreover, the specific surface area was highest with high graphite-N ratio, providing abundant active sites, achieving an energy efficiency 11.77% higher than pristine electrode at 200 mA/cm² [62]. In summary, nitrogen doping has been shown to change the electronic properties of carbon electrode, increase the adsorption of vanadium ions, create defect sites with higher electrochemical activity, and reduce the reaction activation energy, which was determined by the type of nitrogen functional groups [63].

Beyond nitrogen alone, co-doping with other heteroatoms has been explored to achieve synergistic improvements in VRFB electrode performance. For example, N-P co-doped graphite felt achieved a voltage efficiency of 75% at 300 mA/cm², attributed to increased active sites and enhanced vanadium ion adsorption via both N and P functional groups [64]. Similarly, carbon felt co-doped with N and P showed significantly lower charge transfer resistance for the VO²⁺/VO₂⁺ reaction than carbon felt doped only with N or P [65]. For N-S co-doping, graphene or mesoporous carbon modified electrodes showed improved energy efficiency compared to singly doped or undoped samples, which were consistent with enhanced kinetics and wettability due to the combined effect of N and S functional groups [66]. These results suggest that N-P and N-S co-doping can offer stronger catalytic activity than single heteroatom doping by increasing defect density, enhancing adsorption of vanadium species, and improving both conductivity and wettability. However, controlling the ratio, distribution, and bonding environment of the dopants is critical to achieve these benefits.

In summary, nitrogen doping is the dominant approach, while N-P and N-S co-doping demonstrate additional synergistic effects that can further accelerate vanadium redox kinetics. Despite these advantages, challenges related to dopant control and long-term stability in acidic electrolytes still need to be addressed.

1.3.5 Summary of electrode modification strategies

The four main categories of electrode modification, including heat (physical) activation, chemical and electrochemical functionalization, deposition of catalytic nanoparticles, and

heteroatom doping, demonstrate complementary approaches to overcoming the kinetic and transport limitations of VRFB electrodes.

Heat activation primarily enhances surface wettability and increases the number of electroactive sites, though excessive oxidation can compromise conductivity and structural integrity. Chemical and electrochemical functionalization introduce controlled oxygen or nitrogen functional groups to lower charge transfer resistance, but the durability of functional groups in strongly acidic electrolytes remains uncertain. Catalytic nanoparticle deposition provides substantial improvements in reaction kinetics, especially when noble metals or transition metal oxides are employed. However, high cost and particle detachment limit their practical use, whereas non-noble alternatives and transition metal oxides offer more economical solutions but still face stability concerns. Heteroatom doping, particularly nitrogen and its co-doping with phosphorus or sulfur, modifies the electronic structure of carbon and creates new active sites in a cost-effective and scalable way. Nevertheless, achieving precise control over dopant distribution and ensuring long-term stability remain unresolved challenges.

In summary, these strategies have confirmed that electrode modification is indispensable for raising the standard rate constant k_0 , enlarging the electrochemical surface area, and reducing activation and mass transport overpotentials. Among them, heat treatment remains the most widely applied method in both laboratory and industrial settings, owing to its simplicity, low cost, and reproducibility. Nevertheless, most studies do not clearly separate activation, mass transport, and ohmic losses under realistic high current density conditions, and only a few explicitly address the distinct roles of the V^{2+}/V^{3+} and VO^{2+}/VO_2^+ couples on modified electrodes. In addition, trade-offs between activity, durability, scalability, and cost highlight the need for systematic comparisons across modification strategies. Thus, this thesis focuses on heat treatment and investigates in detail its impact on the interfacial kinetics of both half-reactions in VRFBs.

1.4 Research motivation, framework, and contributions

1.4.1 Controversies and knowledge gaps

Heat treatment is widely used as a practical, low-cost route to activate carbon electrodes in VRFBs. It is generally credited with introducing surface oxygen functional groups, improving wettability, and enlarging the ECSA, thereby reducing activation losses and raising achievable current densities [67–69]. However, despite extensive use, several key uncertainties still impede clear design guidelines for high-power operation.

First, the effects of heat treatment are asymmetric between the two half reactions. For the negative V^{2+}/V^{3+} couple, many studies have consistently shown marked kinetic enhancement after heat treatment, with increased k_0 or exchange current density i_0 , reduced charge transfer resistance and mass transport loss at elevated current densities [70–72]. By contrast, the positive VO^{2+}/VO_2^+ couple remains contentious: reports have spanned from moderate improvement to negligible change [73,74], and even inhibition, depending on how surface chemistry is altered by oxidation [75–77]. This divergence underscores a fundamental gap: the role of heat treatment-induced surface functional groups is not uniformly beneficial across both couples, and the mechanistic basis for the contrast has not been fully resolved.

Second, the discussion of overpotential components is still incomplete. Most studies have focused on open-circuit voltage (OCV) or low current densities and therefore have emphasized kinetic effects [78,79]. At higher current densities (up to 200 mA/cm² or more), mass transport loss becomes a major contributor, but it is not fully quantified [80]. Many electrochemical studies have subtracted the ohmic drop and thereby emphasize kinetic differences between electrodes [68,81,82]. While this approach improves comparability, it can underestimate the practical contribution of ohmic resistance, which becomes significant when thicker electrodes are used or at elevated current densities [83,84]. It is therefore essential to determine, at each current density, the separate contributions of charge transfer, mass transport, and ohmic loss. On the positive side, where the reacting species and local acid-base balance differ, comparable and systematic

quantification is even rarer, and cross-comparisons of the positive and negative halves under matched protocols are uncommon [77]. These points all indicate the need for a coherent framework that treats the different overpotential components explicitly.

Third, long-term stability and precipitation-related polarization remain open issues, especially on the positive side. VO_2^+ is thermodynamically unstable in acidic media and is highly sensitive to local pH [85]. Proton consumption and uneven electrode utilization can raise interfacial pH, promoting deprotonated vanadate/vanadyl-sulfate species that condense into hydrated, gel-like deposits and even densify into nanoscale domains [86]. These deposits block the pores, reduce the accessible area, elevate the transport resistance, and degrade the durability [87]. Existing work has largely provided chemical characterizations of electrolyte instability [88–90], but there is a lack of operando, quantitative explanations that link precipitation to performance degradation under realistic operating conditions.

Overall, these gaps point to a need for controlled, half reaction-resolved studies under practical current densities that (1) explicitly compare negative and positive sides under matched heat treatment protocols; (2) separate activation, mass transport, and ohmic contributions; and (3) integrate electrochemical decomposition with physicochemical diagnostics to reveal how surface chemistry governs both performance and stability.

1.4.2 Research framework

To address the above issues, this thesis adopts a symmetric cell framework, and the core elements are:

Half reaction separation via symmetric cells. Using symmetric configurations eliminates interference from the opposite half reaction and enables direct clarity of each couple under well-controlled conditions. This design is validated to resolve the limiting mechanisms on the negative side and then is extended to the positive side to expose precipitation-coupled behavior under realistic loads.

Electrochemical decomposition under operating current densities. Galvanostatic tests are

combined with EIS to separate charge transfer, mass transport, and ohmic contributions across current conditions. This approach enables us to quantify how heat treatment modifies the balance among kinetic, mass transport, and ohmic loss as the dominant contribution shifts with increasing system load. If relevant, a precipitation-related polarization term (“precipitation overpotential”) is operationally defined from deviations between the measured voltage and the sum of EIS-derived components, enabling targeted analysis of deposition-induced penalties.

Kinetic parameter extraction and protocol-robust analysis. For the negative V^{2+}/V^{3+} couple, Tafel analysis is employed to estimate i_0 and charge transfer coefficient α under conditions aligned with cell operation, complementing EIS-derived charge transfer terms. This approach addresses the limitations of protocol-sensitive cyclic voltammetry noted in prior literature. For the positive VO^{2+}/VO_2^+ couple, where precipitation and non-stationary behavior violate Tafel prerequisites, kinetics are instead characterized by small-signal EIS, together with the operational precipitation overpotential.

Physicochemical characterization to bridge structure and function. Scanning electron microscope (SEM) reveals fiber-scale roughening and deposit morphology; X-ray photoelectron spectroscopy (XPS) tracks oxygen functional groups and their evolution; Raman assists in identifying carbon structure and, where applicable, signatures associated with vanadium oxo/vanadyl-sulfate species. These tools enable correlations between surface chemistry/ECSA/wettability and electrochemical loss.

Systematic electrode pairing allows us to extract half-cell behaviors in detail. Four electrode configurations, both electrodes heated, only positive electrode heated, only negative electrode heated, and neither electrodes heated, are systematically compared to quantify asymmetrical effects. Current densities are extended beyond typical commercial operation to observe relevant transport and precipitation conditions at high power densities.

This integrated framework provides a consistent methodological basis to clarify kinetics, mass transport, and ohmic resistance behavior in each half reaction under heat treatment. By

combining electrochemical and physicochemical diagnostics with four systematic conditions, the framework enables controlled, half reaction-resolved evaluation across practical current densities. This methodological platform establishes the foundation on which the subsequent objectives of this thesis are defined.

1.4.3 Objectives and main contributions

(1) Objectives

1. Quantify irreversible loss mechanisms under realistic loads. Explicitly separate charge transfer, mass transport, ohmic, and precipitation-related polarization for each half reaction.
2. Clarify asymmetric heat treatment effects. Determine how thermal activation shifts the balance between the V^{2+}/V^{3+} and VO^{2+}/VO_2^+ half reactions and identify configurations where the treated electrode benefits while the other becomes rate-limiting.
3. Bridge structure changes to performance. Link oxygen functional groups, wettability, ECSA, and fiber-scale morphology to electrochemical metrics, determining which factors govern performance.
4. Define stability boundaries. Determine how symmetric versus asymmetric electrode treatments redistribute polarization, alter local proton availability, and trigger precipitation.
5. Provide mechanistic insights with design implications. Derive pairing strategies and operational windows that support higher power density without introducing instability.

(2) Main contributions

1. Symmetric cell platform with four heat treatment configurations for half-reaction analysis:

A symmetric cell platform with four electrode treatment configurations (both electrodes heated, only the positive electrode heated, only the negative electrode heated, and neither electrode heated) was established and validated for both the V^{2+}/V^{3+} and VO^{2+}/VO_2^+ couples. Under strictly identical cell geometry, flow field, and operating conditions, this platform provides a stable alternative to conventional three-electrode setups and enables systematic, half-reaction-level comparison of positive and negative electrodes, different vanadium valence states, and

different electrode modification strategies.

2. Integrated framework to decompose overpotentials and identify precipitation polarization:

By combining galvanostatic polarization measurements with impedance analysis, this thesis develops a practical framework to separate the total cell overpotential into contributions from charge transfer kinetics, mass transport, and ohmic resistance under realistic current densities. On this basis, an additional “precipitation-related” overpotential is defined from the part of the voltage rise that cannot be explained by these conventional components. This new term is then linked to experimentally observed vanadium-oxide precipitation, providing an operational diagnostic for identifying when and how precipitation begins to dominate cell behavior, especially on the positive side.

3. Quantification of half-reaction asymmetry and ion-selective response to thermal activation:

Under unified conditions (identical electrode substrate, electrolyte composition, flow field, and current density), the kinetic and mass transport behaviors of all four vanadium ions (V^{2+} , V^{3+} , VO^{2+} , VO_2^+) are quantified, demonstrating that the two half-reactions within the same redox couple are not equivalent in terms of reaction rate and mass transport. Building on this, the effect of a single heat treatment protocol is compared between the negative (V^{2+}/V^{3+}) and positive (VO^{2+}/VO_2^+) couples. For the negative couple, both the electrochemically active surface area and the apparent reaction rate increase, whereas for the positive couple the active surface area increases but the apparent reaction rate decreases. This reveals an ion-selective “compensation” profile of thermal activation and shows that enlarging the active surface area does not necessarily lead to faster kinetics, thereby challenging the oversimplified view that more oxygen functional groups always improve reaction rates.

4. Heat treatment design guidelines based on bottleneck-side identification:

Using normalized indicators that combine electronic conductivity, active surface area, and the relative shares of different overpotential components, the four electrode-pairing configurations are compared in a consistent way. This analysis allows the kinetic or mass transport

“bottleneck side” in each configuration to be identified and explains why single-sided heat treatment can lead to mismatched behavior and trigger precipitation earlier, even if the treated electrode itself shows better performance. From these findings, practical heat treatment guidelines are proposed, such as the necessity of activating the positive VO_2^+ reduction side, which can be transferred to other carbon papers and operating conditions in high power vanadium redox flow batteries.

1.5 Thesis structure

Chapter 1 (Introduction): Presents the background, significance, and state of the art in VRFB electrode research. It highlights current controversies and knowledge gaps, and defines the research framework, objectives, and main contributions of this work.

Chapter 2 (Methods): Describes the preparation of heat-treated and not-heated electrodes, the design of symmetric cell configurations, and the electrochemical and physicochemical characterization methods employed.

Chapter 3 (Heat treatment effects on carbon electrodes): Examines the direct impacts of thermal activation on electrode morphology, surface chemistry, wettability, and conductivity. This chapter uses SEM, XPS, Raman, porosity, and contact-angle analyses to establish the structural and chemical foundations for subsequent electrochemical studies.

Chapter 4 (Negative half reaction: $\text{V}^{2+}/\text{V}^{3+}$): Investigates the kinetic and mass transport behaviors of the $\text{V}^{2+}/\text{V}^{3+}$ couple. Using EIS and Tafel analysis, this chapter quantifies the impact of electrode heat treatment under practical current densities.

Chapter 5 (Positive half reaction: $\text{VO}^{2+}/\text{VO}_2^+$): Examines the $\text{VO}^{2+}/\text{VO}_2^+$ couple, with emphasis on precipitation-related instabilities. The analysis introduces the precipitation overpotential and evaluates heat treatment asymmetry under realistic operating conditions.

Chapter 6 (Comparative analysis between $\text{V}^{2+}/\text{V}^{3+}$ and $\text{VO}^{2+}/\text{VO}_2^+$ reaction): Integrates results from both half reactions to establish cross-comparisons, reveal asymmetry in heat treatment effects, and link surface/structural changes to electrochemical performance.

Chapter 7 (Conclusions and perspectives): Summarizes the main findings, highlights the methodological contributions, and provides perspectives for electrode design and high-power operation in VRFB stacks.

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Chapter 2

Methods

2.1 Materials

The carbon electrodes used in this work were carbon paper sheets (39AA, SGL Carbon, Germany) manufactured from PAN precursors and highly graphitized during production. The sheets contained no Polytetrafluoroethylene (PTFE) wet-proofing and no microporous layer, so direct surface modification was feasible. Each sheet had a nominal thickness of 280 μm . Two sheets were stacked to form a single electrode, giving 560 μm before compression and 400 μm after compression. The compression ratio was defined as the compressed thickness divided by the initial thickness and was 71.4%. The geometric area of each electrode was fixed at 1.8 cm $\times$ 1.8 cm, corresponding to 3.24 cm².

Nafion 211 membranes (DuPont, USA) with a thickness of 25 μm were used as the proton exchange membranes. Before cell assembly, the membranes were soaked in deionized water for at least 24 hours to maintain hydration. To ensure consistency across the experiments, no other pretreatment was performed to avoid introducing additional surface modifications.

Two types of vanadium electrolytes were prepared depending on the half reactions. For the negative half reaction involving the $\text{V}^{2+}/\text{V}^{3+}$ couple, the electrolyte contained 1.7 M vanadium ions in 4.3 M H_2SO_4 , which is a common composition used for practical VRFB studies. For the positive half reaction involving the $\text{VO}^{2+}/\text{VO}_2^+$ couple, a lower concentration electrolyte (1.0 M vanadium in 3.0 M H_2SO_4) was employed. The lower concentration was selected to slow the charge transfer process. At higher concentrations, the charge transfer resistance becomes small and the semicircle in the EIS spectrum is difficult to resolve due to fast kinetics. By lowering the vanadium and acid concentration, the charge transfer process could be slowed down, allowing the charge transfer resistance semicircle to be clearly observed and enabling reliable fitting.

Before electrochemical measurements, both electrolytes were conditioned to 50% state

of charge (SOC) with a constant charging current at 200mA/cm² and cut-off voltage was 1.6 V. Initially, the reservoirs contained the commercial symmetric electrolyte mixture of V³⁺ and VO²⁺ in a 1:1 molar ratio (average valence = 3.5+, OCV = 0 V). To obtain the conventional 50% SOC condition (negative side: V²⁺/V³⁺ = 1:1; positive side: VO²⁺/VO₂⁺ = 1:1), the electrolyte was charged by the full one-electron theoretical capacity. The required charge was calculated by coulomb counting according to:

$$Q_{\text{theoretical}} = \frac{F}{3600} \times c \times V \quad (2-1)$$

where $Q_{\text{theoretical}}$ is the total theoretical charge (in Ah), F is Faraday's constant (96485 C/mol), c is the total vanadium ion concentration (mol/L), V is the electrolyte volume (L), 3600 is the conversion factor from coulombs to Ah.

The conditioning process was divided into two stages: (1) the initial mixture was separated into V³⁺ (anolyte) and VO₂⁺ (catholyte) through charging, and (2) the anolyte and catholyte were further charged to reach the states V²⁺/V³⁺ = 1:1 and VO²⁺/VO₂⁺ = 1:1, respectively. This procedure corresponded to a full one-electron transfer per vanadium ion, which equaled 100% of the theoretical capacity. Therefore, the 50% SOC condition was operationally defined and controlled by coulomb counting, rather than inferred from cell potential.

Electrolyte circulation was maintained by two diaphragm pumps (Tacmina, Japan) to suppress flow fluctuations, each delivering a stable flow rate of 20 mL/min to the positive and negative sides. The flow rates were calibrated gravimetrically with an accuracy of ± 0.1 mL/min, and the deviation between the two pumps was kept within $\pm 1\%$ throughout the measurements. To prevent concentration gradients in the reservoirs, a magnetic stirring ball was placed in each tank and driven by an external magnetic stirrer plate, ensuring continuous mixing of the electrolyte. In addition, nitrogen gas (99.999% purity, Iwatani, Japan) was continuously purged into the reservoirs to remove dissolved oxygen and suppress unwanted side reactions during charging.

2.2 Electrode preparation

Two types of electrodes were investigated in this study: not-heated (pristine) electrodes and heat-treated (thermally activated) electrodes. Before any characterization or electrochemical testing, all carbon electrodes were cleaned to remove surface impurities. The only exception was the set of experiments designed to detect precipitation, in which vanadium oxo species and/or vanadyl-sulfate coordination deposits formed on the negative electrode were intentionally preserved for ex-situ observation. The cleaning procedure involved three steps. First, the electrodes were immersed in anhydrous ethanol for 10 min to remove organic residues. Second, the electrodes were transferred to deionized water for 10 min to wash away residual particulates. Finally, the electrodes were dried under vacuum at 60 °C for 2 h. This procedure ensured a reproducible clean surface without introducing structural damage. All not-heated and heat-treated electrodes underwent this cleaning before further use.

For heat-treated electrodes, thermal activation was carried out in a program-controlled muffle furnace (Denkai-Highdental, Japan). The electrodes were inserted into the furnace at room temperature (25 ± 1 °C). The temperature was increased at a rate of 10 °C/min until 500 °C was reached. The electrodes were then held at 500 °C for 12 h in air (21% O₂ and 79% N₂), after which the furnace was turned off and the electrodes cooled naturally to room temperature. Because the carbon paper is very thin, the electrode temperature is expected to rapidly equilibrate with the furnace atmosphere and become nearly uniform throughout its thickness. Consequently, temperature gradients within a single piece of carbon paper during the 12 h dwell were considered negligible, and the heat treatment can be regarded as spatially uniform across the electrode.

This procedure was selected because previous studies have shown that moderate temperature heat treatment in air improves the wettability and surface oxygen functionality of carbon electrodes while preserving structural integrity. Lower temperatures (< 400 °C) are often insufficient to fully activate the surface, whereas higher temperatures (> 600 °C) can cause excessive burn-off and mechanical weakening [1]. In addition to temperature, the treatment

duration also plays a critical role. A shorter dwell time does not provide sufficient oxidation to fully modify the surface, whereas excessively long durations can lead to surface damage and loss of mechanical strength. Therefore, a dwell time of 12 h at 500 °C was chosen as a compromise condition that balances surface activation with structural stability.

After heat treatment, electrodes were stored in sealed desiccators to prevent adsorption of moisture or air contaminants. To minimize variation, electrodes from the same batch of treatment were used together in one set of experiments.

2.3 Symmetric cell configuration

Electrochemical measurements were performed using a symmetric cell specifically designed for half reaction studies. The cell consisted of two identical graphite flow plates with interdigitated channels mounted on an acrylic frame. The channel width and rib width were both 1 mm, the channel depth was 1 mm, and the number of parallel channels was 11 (Fig. 2-1). Two gaskets made of the porous PTFE-perfluoroelastomer (FFKM) composites were used to control electrode compression and prevent electrolyte leakage. Each electrode (3.24 cm² geometric area) consists of two layers of 39AA carbon paper, compressed from 560 μm to 400 μm during assembly. Equal compression was applied to both sides to avoid mechanical asymmetry.

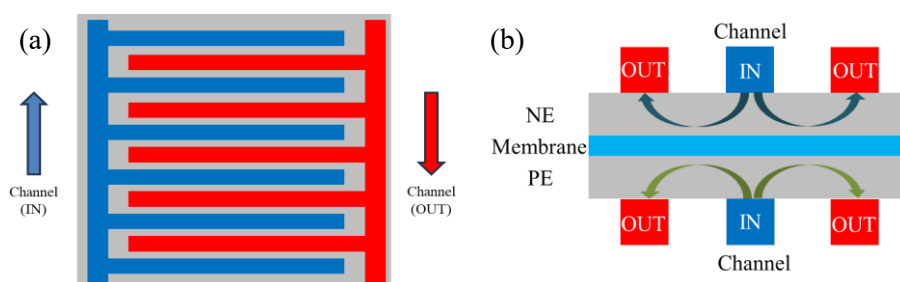


Fig. 2-1 Schematic diagram of the interdigitated flow field (a) top view (b) side view

Two types of symmetric cells were constructed depending on the redox couple under study. In both cases, the same electrolyte reservoir supplied both electrodes, which led to an OCV of 0 V. Electrolyte compositions, SOC conditioning, and operating conditions (flow control,

stirring, N₂ purge) were described in Section 2.1.

(1) For the V²⁺/V³⁺ couple, V³⁺ was reduced to V²⁺ at the negative electrode (NE) while V²⁺ was oxidized to V³⁺ at the positive electrode (PE) during charging (Fig. 2-2a).

(2) For the VO²⁺/VO₂⁺ couple, VO₂⁺ was reduced to VO²⁺ at the NE and VO²⁺ was oxidized to VO₂⁺ at the PE during charging (Fig. 2-2b).

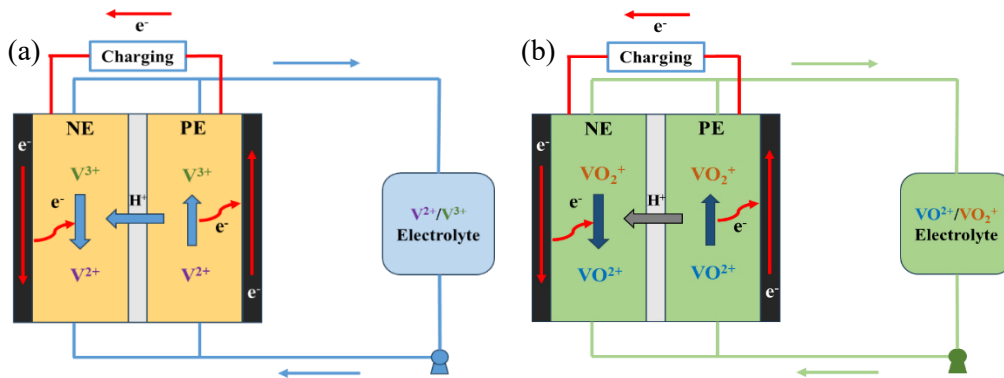


Fig. 2-2 Schematic of the symmetric VRFB configuration (a) V²⁺/V³⁺ (b) VO²⁺/VO₂⁺

This configuration eliminates the influence of cell potential differences and isolates the kinetic and transport behaviors of the individual redox couples.

To study the role of electrode surface treatment, four electrode configurations were tested:

- (1) BH (both heated): both positive and negative electrodes heat-treated
- (2) PNH (positive not heated): only the negative electrode heat-treated
- (3) NNH (negative not heated): only the positive electrode heat-treated
- (4) BNH (both not heated): both electrodes untreated

This arrangement allowed direct comparison between symmetric (BH, BNH) and asymmetric (PNH, NNH) conditions while keeping all other parameters constant. For each configuration, at least three independent cells were assembled and measured to confirm reproducibility and minimize random errors.

2.4 Physicochemical characterization

2.4.1 Scanning electron microscopy and energy-dispersive X-ray spectroscopy

Before electrochemical tests, the surface morphology of not-heated and heat-treated electrodes was examined by scanning electron microscopy (SEM, Hitachi S-3400N, Japan). Samples were cleaned as described in Section 2.2 and mounted on metal stubs using double-sided conductive carbon tape, then imaged at an accelerating voltage of 5 kV (working distance ≈ 4 mm). Elemental analysis was performed by energy-dispersive X-ray spectroscopy (EDX) at 15 kV. At least three regions were analyzed for each sample to ensure representative images.

For post-mortem observation (including precipitation), electrodes were taken from the cell, directly vacuum-dried at 60 °C for 2 h, and examined by SEM-EDX under the same conditions.

2.4.2 Raman spectroscopy

Raman spectra were acquired using a WITec Raman microscope (Oxford Instruments, U.K.) with a 532 nm laser and a 100 $\times$ objective.

For pre-experiment, spectra were recorded over 1000-2000 cm^{-1} with 0.5 s exposure and 10 accumulations per spot. The data processing was performed in OriginPro software. A linear baseline correction was applied to remove background contributions. The spectra were then deconvoluted into two components: the D band ($\sim 1340 \text{ cm}^{-1}$, disorder-induced) and the G band ($\sim 1580 \text{ cm}^{-1}$, graphitic sp^2 carbon). Both peaks were fitted using the Breit-Wigner-Fano (BWF) function to capture the slight asymmetry of the G band [2]. The BWF intensity is given by:

$$I(\omega) = \frac{I_0(1 + \frac{\epsilon}{q})^2}{1 + \epsilon^2} \quad (2-2)$$

with $\epsilon = (\omega - \omega_0)/\Gamma$. Here ω , ω_0 , q , Γ , and I_0 are the Raman shift (cm^{-1}), the spectral peak position (cm^{-1}), the asymmetric factor, the spectral width (cm^{-1}), and the maximum intensity of the BWF spectra (arbitrary units, a.u.), respectively. When $|q| \rightarrow \infty$, the function reduces to a Lorentzian. For consistency across all bands, the D band was also fitted with the same BWF

function, but with q fixed at 1000, making the line shape effectively Lorentzian. From the fitted spectra, the intensity ratio I_D/I_G and peak area ratio A_D/A_G were used as a measure of defect density and degree of graphitization.

For post-mortem analysis (wet state): spectra were recorded over 0-1200 cm^{-1} to identify surface products related to vanadium oxides and sulfate coordination. Peak findings and assignments were also performed in the OriginPro software using the same optical configuration unless otherwise specified.

2.4.3 X-ray photoelectron spectroscopy

The surface chemical composition of not-heated and heat-treated electrodes was analyzed using X-ray photoelectron spectroscopy (XPS, Shimadzu AXIS Supra+, Japan) with Al $K\alpha$ radiation. Survey scans were collected to determine elemental composition, and high-resolution spectra of C 1s and O 1s regions were recorded. A Shirley background correction was applied, and peak fitting was performed using pseudo-Voigt functions with a Gaussian fraction of 0.75 [3].

Because the very intense sp^2 C-C peak at ~ 284.4 eV strongly overlaps with oxidized carbon contributions (C-O, C=O), the C 1s region was not further deconvoluted to avoid over-interpretation. Instead, the O 1s spectra were deconvoluted into C-O and C=O components, which provide more reliable information on oxygen functionalities. The O/C atomic ratio was calculated semi-quantitatively from the integrated areas of O 1s and C 1s peaks, corrected with Scofield sensitivity factors. This ratio was used to compare the relative oxygen content between pristine and heat-treated samples.

2.4.4 Contact angle

Static contact angles were measured by placing a 10 μL droplet of 50% SOC electrolyte ($\text{V}^{2.5+}$ for the negative electrolyte tests or $\text{V}^{4.5+}$ for the positive electrolyte tests) on the electrode surface at 25 ± 1 $^\circ\text{C}$. Images were captured with a digital microscope (Shodensha CT200HD, Japan). The contact angle was determined by the tangent method in ImageJ. Three locations per electrode were measured; values were reported as mean $\pm$ standard deviation.

2.4.5 Porosity

Electrode porosity (ε) was estimated gravimetrically from the bulk density and the true density of the carbon fibers:

$$\varepsilon = \left(1 - \frac{m}{\rho V}\right) \quad (2-3)$$

where m (g) is the electrode mass, ρ (g/cm³) is the true density, and V (cm³) is the electrode volume determined from geometric area and compressed thickness. Three electrodes per condition were measured. This gravimetric method was chosen because it is simple and widely used for fibrous carbon electrodes, providing sufficient accuracy for comparative analysis between not-heated and heat-treated samples.

2.5 Electrochemical measurements

2.5.1 Polarization (I-V) curves

Steady-state polarization (I-V) curves were obtained by a galvanostatic step protocol (Kikusui, Japan). The current density was sequentially increased from 0 to 200 mA/cm² in predefined conditions. At each condition, the cell voltage was recorded after a stabilization period of 60 s, and the average value of the final 10 s was taken as the steady-state potential. This protocol enabled reliable evaluation of the overall cell performance under practical operating conditions. For each electrode configuration, three independent cells were tested to confirm reproducibility.

2.5.2 Electrochemical impedance spectroscopy

EIS was performed using an electrochemical testing system (Solartron, UK). EIS was conducted both at OCV and under the same current densities as the polarization tests. A small AC perturbation (10 mA or 10% of the applied DC current, whichever was larger) was superimposed, and spectra were recorded over a frequency range from 20 kHz to 10 mHz.

The impedance spectra were analyzed using equivalent circuit models appropriate for the two half reactions. Since the asymmetry of charge transfer and mass transport of the V²⁺/V³⁺ symmetric cell was not apparent in the spectra, they were fitted with:

$$R_{\text{ohm}} - [CPE_{\text{ct}} || R_{\text{ct}}] - [CPE_{\text{mt}} || R_{\text{mt}}] \quad (2-4)$$

For the $\text{VO}^{2+}/\text{VO}_2^+$ system, where mass transport asymmetry was more pronounced, the circuit used was:

$$R_{\text{ohm}} - [CPE_{\text{ct}} || R_{\text{ct}}] - [CPE_{\text{mt1}} || R_{\text{mt1}}] - [CPE_{\text{mt2}} || R_{\text{mt2}}] \quad (2-5)$$

Here, R_{ohm} ($\Omega \text{ cm}^2$) is the ohmic resistance, R_{ct} ($\Omega \text{ cm}^2$) is the charge transfer resistance, and R_{mt1} , R_{mt2} ($\Omega \text{ cm}^2$) are the mass transport resistances of the two electrodes, each paralleled with a constant phase element (CPE) to capture non-ideal capacitive behavior.

It is noteworthy that while using two separate kinetic RC elements ($R_{\text{ct}}\text{-}CPE_{\text{ct}}$) might appear more realistic given the asymmetry introduced by different electrode treatments, the spectra were found to be dominated by the not-heated electrode side. Introducing two independent $R_{\text{ct}} - CPE_{\text{ct}}$ branches significantly increased fitting instability and parameter uncertainty. Therefore, a single $R_{\text{ct}}\text{-}CPE_{\text{ct}}$ element was employed to represent the apparent kinetics of the overall cell.

Similarly, although Warburg elements are widely used to represent semi-infinite diffusion, the pore-scale mass transport in porous carbon involves convection-diffusion coupling, which is not well captured by a classical Warburg response. For this reason, the simplified factor $R_{\text{mt}}\text{-}CPE_{\text{mt}}$ was adopted instead. Despite these simplifications, the chosen circuits yielded physically meaningful and stable fitting results, enabling reliable impedance decomposition and accurate calculation of the corresponding overpotentials.

To independently validate the fitted resistances, an apparent cell resistance from polarization curves using the instantaneous slope at each current step could be determined:

$$R_{\text{cell}} = \frac{\Delta U}{\Delta I} = R_{\text{ct}} + R_{\text{mt}} + R_{\text{ohm}} \quad (2-6)$$

where ΔU is the change in cell voltage, V; ΔI is the change in current density, A/cm²; R_{cell} is the total resistance of the cell, $\Omega \text{ cm}^2$.

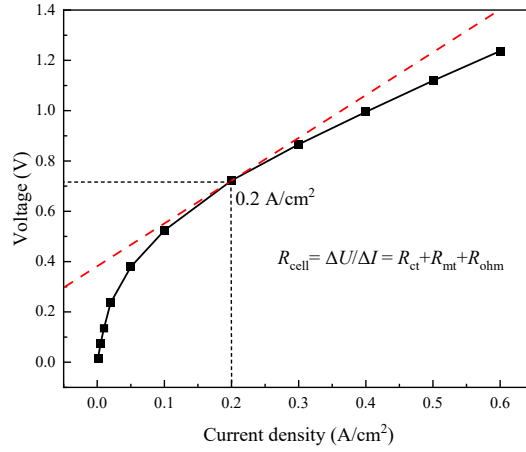


Fig. 2-3 Determination of R_{cell} from the slope of the polarization curve

Figure 2-3 shows the method for obtaining the total resistance R_{cell} from the I-V curve, which can be used as an experimental benchmark for the total resistance obtained by EIS.

2.5.3 Overpotential decomposition

Overpotentials associated with each physical process were obtained by integrating the fitted area-specific resistance as a function of current density i (A/cm^2):

$$\eta_x(I) = \int_0^I R_x(i) di \quad (2-7)$$

where η_x (V) is the overpotential associated with each resistance component; I (A/cm^2) is the applied current density; $R_x(i)$ ($\Omega \text{ cm}^2$) is the resistance obtained from EIS fitting; $x = \text{ct}$, mt , or ohm .

For the $\text{VO}^{2+}/\text{VO}_2^+$ system with two mass transport branches:

$$\eta_{\text{mt}}(I) = \int_0^I [R_{\text{mt1}}(i) + R_{\text{mt2}}(i)] di \quad (2-8)$$

The EIS-derived total overpotential η_{EIS} is then

$$\eta_{\text{EIS}}(I) = \eta_{\text{ct}}(I) + \eta_{\text{mt}}(I) + \eta_{\text{ohm}}(I) \quad (2-9)$$

In practice, $R_x(i)$ is available at discrete DC current steps i_k from EIS. Numerical integration was performed by the trapezoidal rule:

$$\eta_x(i_k) \approx \sum_{k=1}^k \frac{R_x(i_k) + R_x(i_{k-1})}{2} (i_k - i_{k-1}) \quad (2-10)$$

where units are consistent since R_x is in $\Omega \text{ cm}^2$ and i in A/cm^2 , yielding η_x in volts.

The precipitation overpotential was defined for comparison with the directly measured total overpotential η_{tot} in the $\text{VO}^{2+}/\text{VO}_2^+$ system:

$$\eta_{\text{prc}}(I) = \eta_{\text{tot}}(I) - \eta_{\text{EIS}}(I) \quad (2-11)$$

and verification of agreement between η_{tot} and η_{EIS} is presented in Chapter 4 and Chapter 5.

2.5.4 Tafel analysis

Charge transfer overpotentials η obtained from the decomposition above were used to construct Tafel plots:

$$\eta_{\text{ct}} = a + b \log_{10} i \quad (2-12)$$

where η_{ct} is the charge transfer overpotential calculated from EIS, (V); i is the current density (A/cm^2); a is the intercept, (V); b is the Tafel slope, (V/dec). Based on Tafel slope b , the charge transfer coefficient α was calculated using the following relationship:

$$\alpha = \frac{2.303RT}{nFb} \quad (2-13)$$

where 2.303 is the conversion factor between natural logarithms and common logarithms. It is worth noting that the α obtained here is the apparent α of the overall cell, mainly influenced by the slower kinetic side, rather than the true single-electrode charge transfer coefficient.

2.5.5 Electrochemical surface area and standard rate constant

The equivalent double-layer capacitance C_{eff} was obtained by fitting the impedance data using an equivalent circuit model [4]:

$$C_{\text{eff}} = Q^{\frac{1}{\beta}} \left(\frac{R_{\text{ohm}} R_{\text{ct}}}{R_{\text{ohm}} + R_{\text{ct}}} \right)^{\frac{1-\beta}{\beta}} \quad (2-14)$$

where Q is capacitive parameter of the CPE component, $\mu\text{Fs}^{(\beta-1)}/\text{cm}^2$, β is a dimensionless parameter between 0 and 1. From the equivalent capacitance C_{eff} , the effective electrochemical surface area A_{eff} could be calculated as follows:

$$A_{\text{eff}} = \frac{C_{\text{eff}}}{C_s} \quad (2-15)$$

where C_s represents the specific capacitance of the carbon paper electrode, using $23 \mu\text{F}/\text{cm}^2$ (typical $20\text{-}25 \mu\text{F}/\text{cm}^2$ [5,6]). At high sulfuric-acid concentrations ($\geq 1 \text{ M}$), the diffuse layer is highly compressed, and the double-layer capacitance approaches the compact-layer limitation [7]. Consequently, C_s shows only weak dependence on H_2SO_4 in the 3 M and 4.3 M concentration used in $\text{V}^{2+}/\text{V}^{3+}$ and $\text{VO}^{2+}/\text{VO}_2^+$ symmetric cell configuration, respectively. For carbon papers subjected to moderate air heat treatment (500°C for 12 h), previous studies have shown that performance improvement mainly originates from the enhanced wettability, increased oxygen functional groups, and changes in the accessible surface area [1]. Although oxygen functional groups and micropores may slightly affect the intrinsic specific capacitance of carbon materials [8], using the constant C_s remains a practical and effective approach for comparing relative electrochemically accessible areas [9–11]. Therefore, it should be noted that C_s may not be an absolute constant before and after heat treatment, but in this study the same C_s value was used for both conditions to allow a consistent and intuitive comparison of electrochemical surface area (ECSA).

It should be noted that the Brunauer-Emmett-Teller (BET) method was not used to measure the total surface area of the carbon paper. While BET is widely used to quantify the physical specific surface area of porous materials, only a fraction of the gas-accessible area is actually wetted and ion-accessible under flow cell operation. Consequently, increases in BET-derived surface area do not necessarily lead to proportional improvements in reaction kinetics or overpotential, as previous studies have shown that the ECSA derived from double-layer capacitance better represents the usable surface involved in charge transfer for heat-treated carbon electrodes [9]. Therefore, ECSA, along with SEM morphology (Section 2.4.1) and porosity (Section 2.4.5) was used to evaluate the accessible surface generated by heat treatment.

At OCV, the effects of DC load are absent, and the influence of mass transport is minimized. The apparent exchange current density i_0 was first calculated from the charge transfer resistance R_{ct} according to the linearized Butler-Volmer relation [12]:

$$i_0 = \frac{RT}{nFR_{ct}} \quad (2-16)$$

where R is the gas constant, 8.314 J/(mol·K); T is the experimental temperature, 298K; n is the number of electrons transferred in the reaction, 1; F is Faraday's constant, 96485 C/mol.

The reaction rate constant k_0 was determined from the following relationship [13]:

$$k_0 = \frac{RT}{n^2 F^2 A_{eff} C R_{ct}} \quad (2-17)$$

where C is the bulk molar concentration of the reacting vanadium species at 50% SOC in each condition. Thus, C includes only the vanadium reactant concentration (0.85 mol/L for V^{2+}/V^{3+} system and 0.5 mol/L for VO^{2+}/VO_2^+ system).

To enable cross-system comparisons that involve different acid concentrations or different half reactions, a proton-normalized rate constant k_0^* is defined for the VO^{2+}/VO_2^+ reaction (Eq. (1-2)):

$$k_0^* = \frac{k_0}{[H^+]^m} \quad (2-18)$$

where $[H^+]$ is the concentration of protons participating in the reaction and m is the proton reaction order. Following literature on the apparent kinetics of this couple, the proton dependence is taken as first order ($m = 1$) for this normalization [14].

Within a given acid concentration series, $[H^+]$ is treated as constant and raw k_0 is used for the same series trends. For the negative couple V^{2+}/V^{3+} (Eq. (1-1)), no proton term appears in the rate law, so no H^+ correction was applied. To evaluate the concentration of H^+ participating in the reaction, the dissociation formula of H_2SO_4 is listed:



For estimating $[H^+]$ in sulfuric acid electrolytes under the present conditions (25 °C, $c_{H_2SO_4} = 3.0$ M in VO^{2+}/VO_2^+ system), an engineering approximation in which the first dissociation Eq. (2-19a) is effectively complete, whereas the second dissociation Eq. (2-19b) is partial, with a dissociation degree of about 0.33 [15]. Accordingly, the effective proton concentration is estimated as $[H^+] \approx 4.0$ mol/L.

Overall, a normalized rate constant can be defined:

$$k_0^* = \begin{cases} k_0, V^{2+}/V^{3+} \\ \frac{k_0}{[H^+]}, VO^{2+}/VO_2^+ \end{cases} \quad (2-20)$$

with units of k_0^* are cm/s for V^{2+}/V^{3+} and cm/(s · mol/L) for VO^{2+}/VO_2^+ under $m = 1$. This metric is intended for relative comparisons across acid concentrations and half reactions and is not meant to replace the actual rate constant k_0 .

It is worth noting that experiments were conducted in a two-electrode configuration, so the kinetic parameters obtained from EIS represent the apparent behavior of the complete cell rather than that of individual electrodes. The linearized Butler-Volmer relation Eq. (2-16) does not require an explicit value of the charge transfer coefficient α . However, for consistency in deriving k_0 and for comparing conditions (Eq. (2-17)), the common assumption that the anodic and cathodic charge transfer coefficients satisfy $\alpha_a + \alpha_c = 1$ was used. The actual values may deviate from this ideal symmetry, but this assumption provides a standard basis for calculation and for cross-system comparison used in this study.

2.5.6 Estimation of effective ionic resistance

To estimate the ionic resistance associated with ionic transport through the porous carbon electrode, the effective ionic conductivity of the electrolyte-filled pores was calculated using the Bruggeman relation:

$$\kappa_{ele} = \kappa_{ref} \varepsilon^{1.5} \quad (2-21)$$

where κ_{ref} is the ionic conductivity of the bulk electrolyte, S/cm; ε is the porosity of the compressed electrode. The exponent of 1.5 is commonly used for fully saturated, isotropic porous

media and assumes a random distribution of pores. This approximation provides a reasonable estimate of the tortuosity effect in carbon-based fibrous structures [16].

The corresponding area-specific ionic resistance across the electrode thickness t (cm) is expressed as:

$$R_{\text{ele}} = \frac{t}{\kappa_{\text{ele}}} \quad (2-22)$$

with units of $\Omega \text{ cm}^2$. For the porous carbon electrode, this expression represents the effective ionic resistance of the electrolyte phase confined within the porous medium, because ionic current is assumed to be carried only by the liquid-filled pores while the solid carbon matrix is electronically conductive and ionically insulating. The porosity and thickness values used in the calculation were obtained from gravimetric and compression measurements described earlier in this chapter.

The same geometric expression, Eq. (2-22), was also used for the membrane, where κ_{mem} corresponds to the through-plane ionic conductivity of the fully hydrated Nafion membrane, and a Bruggeman correction is not applied. Therefore, both the membrane and the porous electrode follow the same general form of area-specific ionic resistance, but the definition of the effective conductivity differs according to their physical structure and conduction pathways.

In the present work, the ionic contribution to the ohmic resistance is approximated by the sum of the electrolyte ionic resistance of the porous electrode and that of the membrane. Additional contributions from contact resistances solid-electrolyte interfaces are lumped into a residual contact term. The electronic resistance of the carbon matrix and current collectors is neglected compared with the ionic resistance of the membrane and electrolyte and is implicitly included in the lumped contact term. As a result, the estimated ionic resistance is used as an order-of-magnitude reference when interpreting the experimentally measured ohmic resistance rather than as an exact decomposition of ohmic resistance.

2.6 Normalization and parameter definitions

This section describes the normalization strategy used later for cross-comparison between

the V^{2+}/V^{3+} and VO^{2+}/VO_2^+ symmetric cells. The aim is to eliminate dependencies on electrolyte composition and to present charge transfer, mass transport, ohmic, and precipitation phenomena on a common normalized scale.

2.6.1 Charge transfer normalization

Activation comparison is conducted at two complementary levels. At the parameter level, the effective electrochemical surface area A_{eff} represents the accessible reaction interface and is directly compared among electrodes. The corrected apparent standard rate constant k_0^* quantifies the intrinsic kinetics. Their product, $A_{\text{eff}}k_0^*$, reflects the overall kinetic accessibility of the system, combining both the available surface and the local reaction rate.

The exchange current density i_0 was also evaluated from the charge transfer resistance for all conditions; however, it is not used as the primary comparison metric, because its strong dependence on electrolyte concentration. The discussion therefore mainly focuses on the relative trends in $A_{\text{eff}}k_0^*$. All kinetic parameters, including i_0 , represent apparent values in the two-electrode configuration and primarily reflect the slower side of the symmetric cell.

At the overpotential level, the charge transfer overpotential η_{ct} is evaluated by numerical integration of the fitted R_{ct} after separating ohmic and mass transport contributions (see Section 2.5.3). No additional proton correction was applied to η_{ct} to avoid double-counting with the parameter-level normalization. For the positive electrolyte, data at or beyond the precipitation onset current density were excluded to prevent the effects of side reaction.

2.6.2 Mass transport characterization

Mass transport overpotential η_{mt} was obtained by integrating the mass transport component as described in Section 2.5.3. Under steady-state diffusion to a reactive interface, the limiting current density for a first-order consumption of the reacting species is [17]:

$$i_{\text{lim}} = \frac{nFD_{\text{eff}}C_b}{\delta_{\text{eff}}} \quad (2-23)$$

where D_{eff} is the effective diffusion that includes viscosity and porous electrode effects such as

porosity and tortuosity, m²/s; C_b is the bulk concentration of the limiting species, mol/L; and δ_{eff} is the effective diffusion layer thickness that combines the external boundary layer and the intra pore path length, m.

To quantify the mass transport limitation, the η_{mt} was related to the standard diffusion layer model assuming single-electron transfer ($n = 1$) and first-order consumption of the reacting vanadium species at the interface [17,18]:

$$\eta_{\text{mt}}(i) = \frac{RT}{F} \ln \left(\frac{1}{1 - \frac{i}{i_{\text{lim}}}} \right) \quad (2-24)$$

where i is the applied current density, A/cm²; i_{lim} is the limiting current density. Thus, it can be rearranged as:

$$i = i_{\text{lim}} [1 - \exp \left(-\frac{F}{RT} \eta_{\text{mt}} \right)] \quad (2-25)$$

An apparent limiting current was then computed at each current density within the pre-precipitation window as:

$$i_{\text{lim}}^{\text{app}}(i) = \frac{i}{1 - \exp \left[-(F/RT) \eta_{\text{mt}}(i) \right]} \quad (2-26)$$

It is noted that $i_{\text{lim}}^{\text{app}}$ is an apparent limiting current density calculated from the η_{mt} at each load. It represents the effective transport capability under the actual structural and operating conditions, including wetting, pore accessibility, and local convection. In contrast to the theoretical i_{lim} , which is constant for a given experimental condition and is not affected by applied current, $i_{\text{lim}}^{\text{app}}$ can vary with the applied current because of current-dependent phenomena.

For cross-system capability comparison, based on the Eq. (2-26), the apparent mass transport coefficient is defined as:

$$k_m^{\text{app}} = \frac{D_{\text{eff}}}{\delta_{\text{eff}}} = \frac{i_{\text{lim}}^{\text{app}}}{nFC_b} \quad (2-27)$$

where C_b is taken as the bulk concentration of the reacting vanadium species at the operating SOC ($C_b = C_{V^{2+}} = C_{V^{3+}}$ for the negative electrolyte and $C_b = C_{VO^{2+}} = C_{VO_2^+}$ for the positive

electrolyte). Here, k_m^{app} is dependent on the applied current: although D_{eff} is governed by the porous microstructure and treated as approximately constant over the measurement window, δ_{eff} is a load-induced parameter depending on concentration gradients, wetting, and dispersion. Thus, $i_{\text{lim}}^{\text{app}}$ (and thus k_m^{app}) may change with current density even if D_{eff} does not. On the $\text{VO}^{2+}/\text{VO}_2^+$ side, sufficiently high current densities can induce local proton depletion, raise the interfacial pH, and trigger precipitation. To exclude this chemistry-coupled region, k_m^{app} was evaluated at current densities below the precipitation onset, where protons remain in large excess, the electrolyte composition is effectively constant, and the limiting behavior arises solely from transport of vanadium species. Therefore, H^+ concentration correction was not applied. Data beyond the onset would cause an apparent k_m affected by precipitation and were not used for comparison.

This approach isolates the intrinsic influence of electrode structure and wettability on the effective diffusivity and diffusion layer thickness, while avoiding interference from precipitation or proton-depletion effects. The parameter k_m^{app} serves as a physically meaningful, system-level indicator that enables direct comparison of intrinsic mass transport capability across different electrode and electrolyte conditions.

2.6.3 Ohmic correction

The total R_{ohm} obtained from the high frequency intercept of EIS spectra is decomposed as:

$$R_{\text{ohm}} = R_{\text{ele}} + R_{\text{mem}} + R_{\text{con}} \quad (2-28)$$

where R_{ele} , R_{mem} , and R_{con} are the resistance of electrolyte phase within the porous electrodes, membrane resistance, and electrode-interfacial contact resistance, $\Omega \text{ cm}^2$, respectively.

Among these components, R_{ele} and R_{mem} depend strongly on the ionic conductivity of the supporting electrolyte and the membrane, whereas R_{con} depends primarily on assembly pressure, electrode morphology, and surface wetting, and is therefore treated as independent of acid concentration [19]. Accordingly, direct comparison of R_{ele} and R_{mem} across different

electrolyte concentrations (3.0 M and 4.3 M H₂SO₄) is not meaningful without correcting for the dependence on conductivity.

To eliminate this effect, the conductivity-normalized ohmic resistance was defined as:

$$R_{\text{ohm}}^* = \frac{R_{\text{ele}} \cdot \kappa_{\text{ele}}}{\kappa_{\text{ele,ref}}} + \frac{R_{\text{mem}} \cdot \kappa_{\text{mem}}}{\kappa_{\text{mem,ref}}} + R_{\text{con}} \quad (2-29)$$

where κ_{ele} and κ_{mem} are the effective bulk and membrane ionic conductivities, S/cm; $\kappa_{\text{ele,ref}}$ and $\kappa_{\text{mem,ref}}$ are their corresponding reference values. The ratio ($\kappa/\kappa_{\text{ref}}$) rescales the electrolyte and membrane related resistances to a common standard while keeping R_{con} unchanged.

In this study, κ_{ref} was chosen as the harmonic mean of the ionic conductivities at 3.0 M and 4.3 M H₂SO₄ to provide a neutral comparison scale because R_{ele} and R_{mem} are proportional to $1/\kappa$ [19].

$$\kappa_{\text{ref}} = \frac{2}{\frac{1}{\kappa_{3.0}} + \frac{1}{\kappa_{4.3}}} \quad (2-30)$$

The resulting R_{ohm}^* thus removes the variation caused by differences in acid concentration or membrane hydration, allowing cross-comparison between the symmetric cells.

2.6.4 Normalization summary

To further unify the relative relationship between overpotentials and enable cross-system comparisons (see Chapter 6), the fractional contribution of each overpotential to the total overpotential is defined as:

$$f_{\text{ct}} = \frac{\eta_{\text{ct}}}{\eta_{\text{tot}}} \quad (2-31a)$$

$$f_{\text{mt}} = \frac{\eta_{\text{mt}}}{\eta_{\text{tot}}} \quad (2-31b)$$

$$f_{\text{ohm}} = \frac{\eta_{\text{ohm}}}{\eta_{\text{tot}}} \quad (2-31c)$$

$$f_{\text{prc}} = \frac{\eta_{\text{prc}}}{\eta_{\text{tot}}} \quad (2-31d)$$

where η_{ct} , η_{mt} , η_{ohm} and η_{prc} are obtained directly from EIS decomposition and numerical

integration (see Section 2.5.3). These fractions express the relative shares of charge transfer, mass transport, ohmic, and precipitation related losses in the total overpotential, enabling straightforward comparison of how each contribution changes under different electrode and electrolyte conditions.

2.7 Summary

This chapter established a comprehensive experimental protocol and a common normalization scheme to compare the V^{2+}/V^{3+} and VO^{2+}/VO_2^+ half reactions. Symmetric cells were employed to isolate half reaction behavior while geometry, compression, flow rate, and membrane were held constant. Electrolytes were conditioned coulombically to 50% SOC.

To distinguish the effects of heat treatment on performance, four symmetric configurations (BH, PNH, NNH, BNH) were tested. Not-heated and heat-treated electrodes were characterized by SEM-EDX, Raman, XPS, contact angle, and gravimetric porosity to provide context for wettability, functional groups, and accessible ECSA. Each measurement was repeated three times to ensure reproducibility. Polarization step tests and EIS at OCV and under load were analyzed with simple and stable circuits specific to each half reaction. From the fitted area specific resistances, charge transfer, mass transport, and ohmic contributions were obtained by numerical integration of $R_x(i)$.

A unified normalization was applied to remove the influence of electrolyte concentration, so the remaining trends reflect intrinsic electrode reactions of vanadium ions. Kinetics were compared via ECSA-based k_0 (with proton-normalized k_0^* only when needed), transport capability was quantified by the apparent mass transfer coefficient k_m^{app} , and ohmic loss was referenced to common conductivities. For cross-system comparison, overpotential components were analyzed at identical operating points, and their fractional shares f_i ($i = ct, mt, ohm, prec$) represent how charge transfer, transport, ohmic, and precipitation losses contribute to the overall polarization. This framework provides a unified and physically grounded platform to compare intrinsic transport and reaction characteristics across electrode treatments and between the two

vanadium half reactions.

Overall, this chapter defined the materials, cell designs, measurements, and analysis procedures that support the study. The framework enables reproducible experiments and interpretation of the V^{2+}/V^{3+} and VO^{2+}/VO_2^+ systems in the chapters that follow, clarifying clear performance limitations to charge transfer, mass transport, ohmic or precipitation effects.

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Chapter 3

Heat Treatment Effects on Carbon Electrodes

3.1 Introduction

This chapter examines how heat treatment in air (500 °C for 12 h, heating rate 10 °C/min, natural cooling) modifies the structure and surface properties of a commercial PAN-based, highly graphitized carbon paper (SGL 39AA). These electrodes were used throughout this study as the porous carbon electrodes in VRFBs. The objective is to establish the material characterization foundation for the electrochemical analyses presented in later chapters.

The focus is on morphology, surface chemistry, wettability, and porosity, because these properties directly influence the effective ECSA, the intrinsic reaction rate constant (k_0), and the transport of electrolyte within the porous electrode network. By systematically comparing pristine (not-heated) and heat-treated electrodes, this study elucidates how the structural and chemical modifications induced by thermal activation govern the subsequent electrochemical performance.

This chapter is motivated by two sets of symmetric cell experiments. One set of symmetric cells isolated the negative half reaction (V^{2+}/V^{3+}) in 1.7 M vanadium with 4.3 M H_2SO_4 at 50 % SOC. Another set of symmetric cells isolated the positive half reaction (VO^{2+}/VO_2^+) in 1.0 M vanadium with 3.0 M H_2SO_4 at 50 % SOC. In both cases, the same electrode material (SGL 39AA) and interdigitated flow fields were used. Here, “not-heated” refers to the pristine carbon paper, while “heat-treated” refers to the electrode after the above 500 °C air treatment.

The structure of this chapter is as follows. Section 3.2 presents SEM observations of binder removal, pore opening, and surface roughening. Section 3.3 describes Raman spectroscopy and XPS results that reveal changes in carbon disorder and oxygen functionalization. Section 3.4 reports wettability measurements with both negative and positive electrolytes, together with porosity calculations. Section 3.5 integrates these results to explain their implications for electrochemical performance in symmetric cell studies. Finally, Section 3.6 summarizes the main

findings and highlights their relevance for electrode design in VRFBs.

3.2 Morphology

The morphology of the not-heated and heat-treated SGL 39AA carbon paper electrodes was examined by SEM.

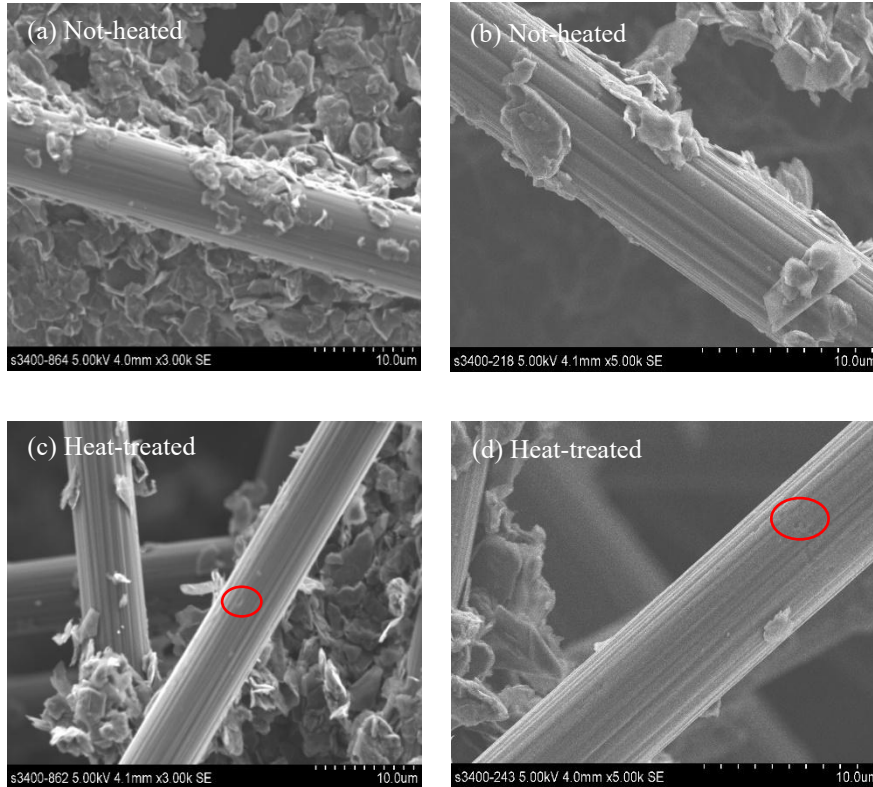


Fig. 3-1 SEM images of carbon paper (a) not-heated, 3000 $\times$ (b) not-heated, 5000 $\times$ (c) heat-treated, 3000 $\times$ (d) heat-treated, 5000 $\times$

Fig. 3-1 (a, b) shows that the not-heated carbon fibers with binder material clearly visible in the inter-fiber junctions and inter-layer regions. At lower magnification, the overall structure appears dense and compact, with fiber-to-fiber contact points covered by binder. At higher magnification, the carbon fibers display relatively smooth surfaces, with only occasional irregularities and small protrusions. These features are consistent with the highly graphitized, polyacrylonitrile (PAN)-based origin of SGL 39AA [1].

Fig. 3-1 (c, d) shows pronounced changes on carbon electrodes after heat treatment at 500 °C in air for 12 h. At low magnification, the electrode structure appears more open, with binder material removed from the inter-fiber junctions. This indicates partial thermal decomposition of the binder, which reduces the extent of fiber-to-fiber adhesion. At higher magnification, the surfaces of individual fibers become visibly rougher, with numerous round pits and etched areas appearing on what were originally smooth fiber surfaces, as marked in the figure. These pits are likely the result of localized oxidation and partial combustion of the carbon surface under air atmosphere, which would thereby increase surface roughness. According to the Wenzel equation, once the surface becomes intrinsically more wettable due to oxidation, the enhanced roughness further amplifies this wettability, facilitating an increase in ECSA [2]. The combined effect of binder removal and surface etching increases accessible pore volume, exposes a larger fraction of the surface to the electrolyte, and reduces air pockets at the electrolyte-carbon interface, suppressing Cassie-Baxter type wetting and promoting a more homogeneous contact [3].

The opening of blocked pores and the creation of additional micro-scale roughness are expected to enhance electrolyte penetration and to expand the geometrically available surface area. However, it should also be noted that such changes can weaken the internal mechanical structure of the electrode. Previous reports have shown that excessive binder decomposition reduces inter-fiber strength, leading to structural fragility [4]. In experimental electrodes, the treatment parameters are selected to balance the removal of inactive binder against the preservation of overall integrity.

The SEM results thus provide direct evidence that heat treatment modifies the morphology of SGL 39AA in two major ways: (1) decomposition of binder and consequent pore opening at the network scale, and (2) creation of surface roughness and pits at the fiber scale. Both effects together contribute to an enlarged electrochemically active area, which will later be quantified by capacitance analysis and related to improved charge transfer kinetics.

3.3 Surface chemistry

This section characterizes how the 500 °C air treatment changes the surface chemistry of SGL 39AA. Raman spectroscopy was used to identify changes in carbon disorder and graphitic order, and XPS was used to quantify oxygen incorporation and bonding environments. Together, these measurements establish whether the treatment primarily introduces edge and defect sites, oxygen functional groups, or both, which in turn influence wettability, ECSA, and charge transfer behavior discussed later.

3.3.1 Raman spectroscopy

Raman spectra (1000-2000 cm^{-1}) were collected on pristine (not-heated) and heat-treated electrodes, which are shown in Fig. 3-2, Table 3-1, and Table 3-2.

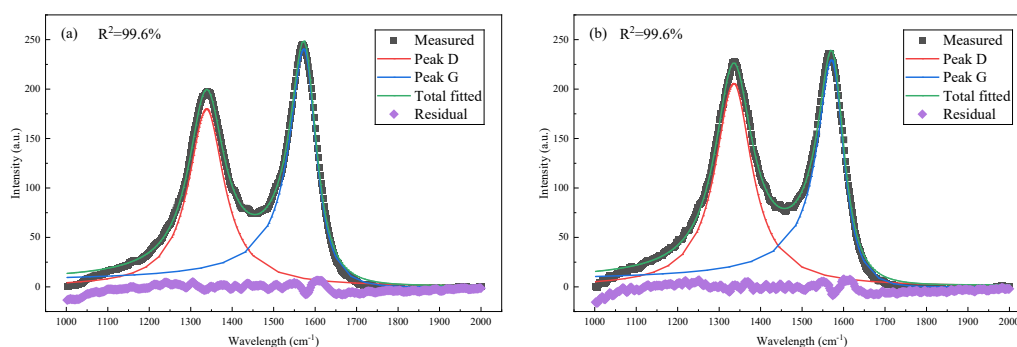


Fig. 3-2 Fitted Raman peaks (a) not-heated; (b) heat-treated

Table 3-1 Raman fitted parameters of the not-heated carbon electrode

	Wavelength (cm^{-1})	FWHM (cm^{-1})	Area (a.u.)	Intensity (a.u.)
D peak	1338.04 ± 0.58	103.63 ± 1.16	27123.67 ± 359.74	179.77 ± 1.18
G peak	1577.65 ± 0.38	80.75 ± 0.74	31580.72 ± 352.62	236.30 ± 1.25

Table 3-2 Raman fitted parameters of the heat-treated carbon electrode

	Wavelength (cm^{-1})	FWHM (cm^{-1})	Area (a.u.)	Intensity (a.u.)
D peak	1335.05 ± 0.53	107.68 ± 1.12	32118.82 ± 415.30	205.58 ± 1.21
G peak	1576.58 ± 0.41	81.39 ± 0.81	31173.44 ± 328.01	224.36 ± 1.29

Using a Breit-Wigner-Fano (BWF) line shape, the D and G peaks were well separated ($R^2 = 99.6\%$). The not-heated sample shows the expected G band near $\sim 1580 \text{ cm}^{-1}$ (sp^2 in-plane vibration) and the D band near $\sim 1340 \text{ cm}^{-1}$ (disorder or defect-activated mode). After heat treatment, the D/G intensity ratio (I_D/I_G) increases from 0.76 to 0.92 (+21.1%), and the D/G area ratio (A_D/A_G) increases from 0.85 to 1.03 (+21.2%). The I_D/I_G and A_D/A_G show the same trend, indicating the accuracy of the fitting method. The G band position shifts slightly by -1.07 cm^{-1} and its full width at half maximum (FWHM) broadens by $+0.64 \text{ cm}^{-1}$. These modest shifts indicate an increase in defect-related scattering while the material remains in a low-to-intermediate defect state rather than full amorphization [5]. In other words, the air treatment generates additional defects and edge sites and shallow surface etching without destroying the overall graphitic framework [6]. This interpretation is consistent with the SEM observations of surface pits and roughening.

3.3.2 X-ray photoelectron spectroscopy

XPS further resolves the oxygen content and bonding states introduced by air treatment. To assess whether heat treatment introduces impurity elements, full survey spectra were collected, as shown in Figure 3-3.

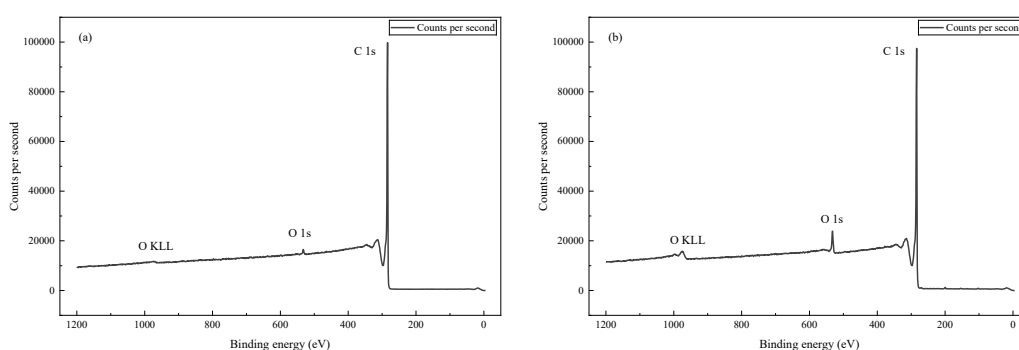


Fig. 3-3 The raw data of full XPS survey spectra (a) not-heated (b) heat-treated

Fig. 3-3 shows that both spectra are dominated by a strong C 1s peak ($\sim 285 \text{ eV}$) and an O 1s peak ($\sim 530 \text{ eV}$). In addition, a small peak near $980\text{-}990 \text{ eV}$ is observed, which can be

assigned to the O KLL Auger transition [7]. After heat treatment, the O 1s peak increases markedly, consistent with the introduction of additional oxygen functional groups, and the O KLL Auger feature becomes more pronounced. No additional elemental signals are detected, confirming that the carbon paper surface consists only of C and O species before and after annealing.

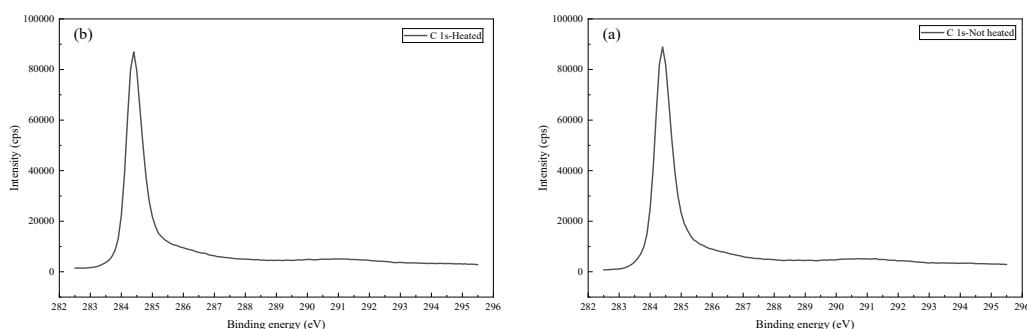


Fig. 3-4 C 1s spectra (a) not-heated; (b) heat-treated

Generally, the quantitative analysis of oxygen functional groups is often performed by fitting the C 1s peak [8]. Although C 1s spectra were also collected, Fig. 3-4 shows the peaks are dominated by a very sharp asymmetric sp^2 C-C component at ~ 284.4 eV with a strong $\pi-\pi^*$ satellite near 291-292 eV. In comparison, the oxidized-carbon contributions (C-O, C=O, O-C=O at 285.5-288.5 eV) are very weak and strongly overlapped with the main sp^2 peak. This makes multi-peak deconvolution of C 1s highly non-unique and prone to overfitting, especially at the relatively low oxygen concentrations observed here. Therefore, the C 1s region is not further fitted; instead, its integrated area is used together with O 1s to calculate the O/C atomic ratio. The identification of oxygen functional groups was based on the O 1s high-resolution spectra, which provides a more reliable separation of C-O and C=O environments. Complementary Raman spectroscopy is also employed to characterize the carbon structural disorder as noted above.

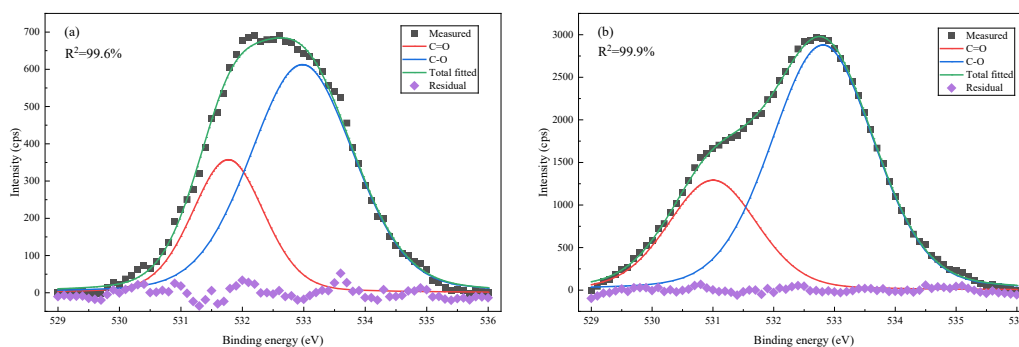


Fig. 3-5 O 1s XPS spectra and peak fitting of carbon paper: (a) not-heated and (b) heat-treated

Thus, O 1s spectra were fitted to identify the carbon surface oxygen functional groups. The spectra were background-corrected by the Shirley method and fitted with pseudo-Voigt line shapes with a fixed Gaussian fraction to ensure consistency across samples. Fig. 3-5 shows that the O 1s spectra are well described by two components, assigned to C=O and C-O functional groups, and the overall fitting quality is good with a high R^2 and low residuals. Importantly, the C=O contribution remains smaller than that of C-O both before and after treatment, suggesting that oxygen incorporation occurs concurrently in different bonding environments.

Table 3-3 Fitted parameters of O 1s (not-heated)

Component	Binding energy (eV)	FWHM (eV)	Area (a.u.)	Relative %
C=O	531.77 ± 0.24	1.37 ± 0.07	568.26 ± 210.95	28.97 ± 8.80
C-O	532.98 ± 0.06	1.99 ± 0.13	1411.64 ± 251.56	71.03 ± 8.80

Table 3-4 Fitted parameters of O 1s (heat-treated)

Component	Binding energy (eV)	FWHM (eV)	Area (a.u.)	Relative %
C=O	531.00 ± 0.06	1.73 ± 0.03	2581.18 ± 202.92	27.86 ± 0.69
C-O	532.81 ± 0.02	1.99 ± 0.02	6656.64 ± 247.52	72.14 ± 0.69

Table 3-3 and Table 3-4 show the detailed fitting results with uncertainties. The reported uncertainties reflect only the statistical component, such as baseline noise and fitting errors. According to [9], the systematic uncertainty of XPS is typically on the order of 5-10% due to

background shapes, sensitivity factors, and instrument response. Since all measurements in this study were performed within the same batch under identical conditions, such systematic bias is expected to be largely common-mode and is therefore not explicitly included.

Based on the integrated areas of the C 1s and O 1s peaks, the O/C atomic ratio was calculated as 0.0087 ± 0.0001 (not-heated) to 0.0438 ± 0.0001 (heat-treated), i.e., about 5.0 $\times$ higher. High-resolution O 1s spectra, fitted with C=O and C-O components, reveal that both before and after treatment the C-O contribution remains larger than C=O, but the heat-treated sample exhibits: (1) a -0.17 eV shift of binding energy in the C-O peak with nearly unchanged width, and (2) a larger -0.77 eV shift and a noticeable broadening (+0.36 eV) in the C=O component. This indicates that C=O groups undergo more pronounced rearrangement during heat treatment, while C-O groups remain comparatively stable. These changes indicate the formation and reorganization of oxygen functional groups across a distribution of chemical environments, consistent with mild oxidative functionalization at defects and edges [10].

From a mechanistic perspective, the combined Raman and XPS results support a picture in which air treatment creates more defect and edge sites and introduces oxygen functional groups (C-O and C=O). These changes matter for electrochemistry in two ways. First, they increase surface polarity, hydrophilicity and improve electrolyte infiltration (quantified in Section 3.4 via contact angles for both negative and positive electrolytes) [11], which promotes uniform access to the porous network. Second, they modify interfacial charge transfer sites and intrinsic reaction rates. In later chapters, the different kinetic effects of this oxygen-containing and defective surface on V^{2+}/V^{3+} and VO^{2+}/VO_2^+ couples will be demonstrated and analyzed.

3.4 Wettability and porosity

Wettability and porosity are key material properties that govern electrolyte infiltration and transport in porous electrodes. In VRFB electrodes, sufficient wetting is essential to ensure that the electrolyte can penetrate the fiber network and access the available electrochemically active surface. Porosity, on the other hand, determines the volume fraction available for

electrolyte transport. Together, these parameters strongly influence the effective ECSA, ion transport, and overall electrochemical performance.

3.4.1 Wettability

Contact angles were measured using vanadium electrolytes to assess the wetting behavior of not-heated and heat-treated carbon papers. Figure 3-6 shows representative images for both negative electrolyte (V^{2+}/V^{3+} , 1.7 M vanadium in 4.3 M H_2SO_4) and positive electrolyte (VO^{2+}/VO_2^+ , 1.0 M V in 3.0 M H_2SO_4).

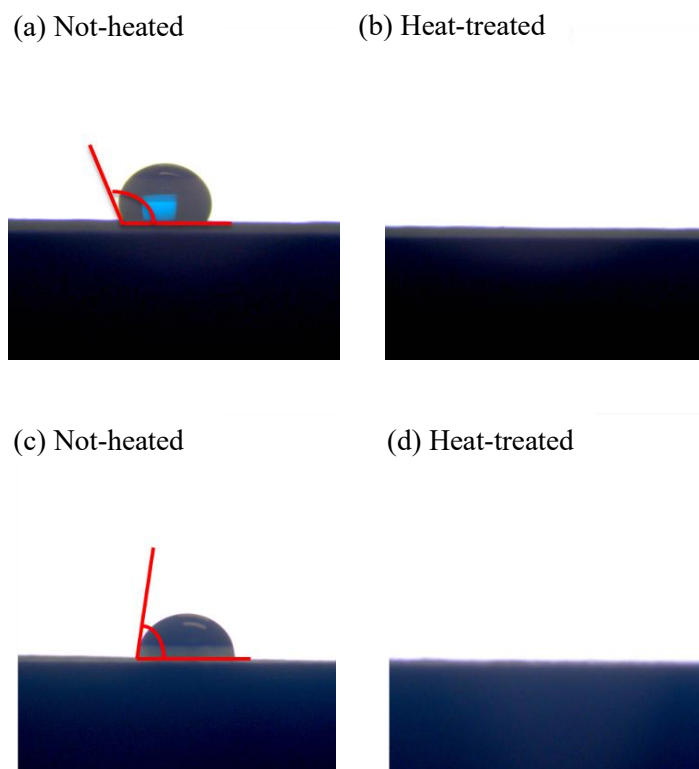


Fig. 3-6 Contact angle images of electrodes (a) not-heated, negative electrolyte (b) heat-treated, negative electrolyte (c) not-heated, positive electrolyte (d) heat-treated, positive electrolyte

On the not-heated electrode, the negative electrolyte ($V^{2.5+}$) exhibits a contact angle of $113.6^\circ \pm 4.3^\circ$, confirming strong hydrophobicity. For the positive electrolyte, the contact angle is also large ($79.2^\circ \pm 4.1^\circ$), indicating similarly poor wetting. This difference in contact angles

between the negative and positive electrolytes may be attributed to the intrinsic properties of the vanadium ions and the different acid concentrations used in the two electrolytes. On the heat-treated electrode, the droplet is immediately absorbed for both electrolytes, so no measurable contact angle can be recorded. This indicates a transition from hydrophobic to highly hydrophilic behavior.

The dramatic improvement in wettability can be attributed to two concurrent changes induced by heat treatment: (1) the development of surface roughness, as observed in SEM, which enhances liquid spreading; (2) the introduction of oxygen functional groups, as confirmed by XPS, which increase surface polarity. These changes ensure rapid electrolyte penetration into the porous network, improving utilization of the fiber surfaces.

3.4.2 Porosity

To estimate the porosity of the carbon electrode, a simplified method based on the ratio of pore volume to total volume was used. Measurements were repeated 3 times and were reported as mean $\pm$ standard deviation.

The porosity ε is given by [12]:

$$\varepsilon = \left(1 - \frac{m}{\rho V}\right) \quad (3-1)$$

where m is the mass of the carbon paper sample (g), ρ is the density of the carbon fiber sample (g/cm^3) and V is the total volume of the carbon paper sample (cm^3).

According to the manufacturer's specifications for 39AA, the not-heated electrode exhibits a nominal porosity of 89%. Based on measurements of the electrode's dimensions (length, width, and thickness) and mass, the actual density of the material was calculated as about $1.7 \text{ g}/\text{cm}^3$, which is close to the range $1.75\text{-}2.00 \text{ g}/\text{cm}^3$ of the carbon fiber [13]. In the symmetric cell assembly, two sheets of carbon paper were stacked on each side of the membrane (i.e., two layers per electrode). The total compressed thickness of one electrode side was set by a $400 \text{ }\mu\text{m}$ gasket, corresponding to $200 \text{ }\mu\text{m}$ thickness per single carbon paper layer after compression. According to Eq. (3-1), the porosity after compression of not-heated carbon electrode is $0.857 \pm$

0.006 while the heat-treated one is 0.886 ± 0.003 .

In addition to geometrical interpretation, porosity also influences the effective ionic conductivity of the electrolyte inside the porous electrode. According to the Bruggeman relation, the effective conductivity (κ_{eff}) scales with porosity as:

$$\kappa_{\text{eff}} = \kappa \varepsilon^{1.5} \quad (3-2)$$

where κ is the bulk electrolyte conductivity and the exponent (≈ 1.5) accounts for tortuosity effects in random porous media. Using this approximation, the increase in porosity from 0.857 to 0.886 corresponds to an estimated $\sim 5\%$ improvement in effective ionic conductivity within the electrode, thereby modestly lowering the ohmic resistance. While the change is small compared with the dramatic enhancement in wettability, it still contributes to reducing ionic conduction losses, particularly under high current operation where ohmic drop is magnified.

It should be noted that while porosity and wettability strongly affect ionic conduction, electronic conduction through the carbon fiber network remains essentially intact. However, heat treatment does induce partial binder loss, which reduces some fiber-to-fiber contact points. Under the present treatment conditions, this effect is relatively minor compared with the high intrinsic conductivity of the carbon fibers, so the overall electronic conduction is not significantly impaired [14].

3.5 Summary

The previous characterization results collectively demonstrate that air heat treatment at 500 °C fundamentally alters the morphology, surface chemistry, and transport properties of the carbon paper electrodes. These modifications can be grouped into three categories: (1) structural rearrangements, including binder decomposition and fiber surface roughening; (2) chemical changes, primarily the incorporation of oxygen functional groups and the creation of edge and defect sites; and (3) transport-related improvements in wettability and porosity. This section integrates these findings and discusses their combined implications for electrochemical performance in VRFB electrodes.

At the structural level, SEM observations reveal that heat treatment removes a portion of the binder that normally adheres to fiber junctions and blocks pores. This decomposition of binder opens previously obstructed flow pathways and exposes additional fiber surface. At the same time, localized etching of the fiber surfaces produces round pits and rough features that enlarge the geometrically accessible surface area. While such changes could, in principle, weaken the mechanical integrity of the network, under the present conditions the electrode retains sufficient mechanical integrity to remain functional. Importantly, the increased surface roughness provides more active sites for charge transfer reactions and increases effective ECSA.

Surface chemistry analysis supports this interpretation. Raman spectroscopy shows an increase in disorder, as indicated by the higher D/G ratio, consistent with the creation of new edge sites and defect domains. XPS analysis reveals a roughly five-fold increase in the surface O/C ratio, with O 1s spectra confirming the formation of C-O and C=O functional groups. These oxygen functional groups increase surface polarity and hydrophilicity, which not only facilitates electrolyte infiltration but also introduces new catalytic sites that can enhance charge transfer kinetics. The combined rise in disorder and oxygen functionality thus provides two mechanisms for improving electrode activity: greater availability of reaction sites and improved interfacial electron transfer characteristics.

Mass transport related properties are also substantially improved. Contact angle measurements show that not-heated 39AA is strongly hydrophobic toward both negative (V^{2+}/V^{3+}) and positive (VO^{2+}/VO_2^{+}) electrolytes, with contact angles of 113.6° and 79.2° , respectively. After heat treatment, both electrolytes are instantaneously absorbed, reflecting a transition to highly hydrophilic behavior. This change arises from the combination of increased surface polarity (due to oxygen functional groups) and increased roughness (due to fiber etching), both of which promote rapid liquid spreading. Improved wettability ensures that the electrolyte can penetrate the porous network more uniformly, reducing the risk of locally underutilized areas and improving access to the internal fiber surfaces.

Porosity analysis complements these findings. The slight increase in porosity from 0.857 to 0.886 corresponds to an estimated ~5% enhancement in the effective ionic conductivity inside the porous electrode, according to the Bruggeman relation. Although this increase is modest compared with the dramatic improvement in wettability, it still contributes to lowering ionic conduction losses, particularly at high current density where ohmic drop becomes significant. In contrast, electronic conduction through the carbon fiber network remains largely intact, with only minor reductions in fiber-to-fiber contact due to binder loss. Thus, heat treatment improves ionic transport without significantly impairing electronic pathways.

Overall, these results show that heat treatment transforms SGL 39AA from a hydrophobic, binder-rich material into a more open, defect-rich, and hydrophilic electrode. These changes provide a larger accessible surface area, a higher density of reactive sites, improved wettability, and slightly enhanced porosity, which together form the basis for the improved electrochemical performance discussed in later chapters. These material-level changes explain why heat-treated electrodes exhibit reduced charge transfer resistance, faster kinetics, and better tolerance to high current operation in symmetric VRFB cells. The link between these structural and chemical changes and the electrochemical behaviors of the V^{2+}/V^{3+} and VO^{2+}/VO_2^+ couples will be quantitatively examined in Chapters 4 and 5.

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Chapter 4

Electrode Heat Treatment in Symmetric Cells: V^{2+}/V^{3+} Half Reaction

4.1 Introduction

In this chapter, the kinetic and mass transport behaviors of the negative half reaction (V^{2+}/V^{3+}) in VRFBs are systematically investigated by employing symmetric cell configurations. Unlike full cell tests, where the positive and negative half reactions are strongly coupled and electrode/electrolyte asymmetry complicates mechanistic interpretation, symmetric cells enable the isolation of a single half reaction under controlled conditions [1]. This configuration eliminates the influence of positive electrolyte half reaction (VO^{2+}/VO_2^+), thereby allowing a more direct evaluation of intrinsic electrode performance [2]. By keeping the electrolyte at 50% state of charge and using a geometrically symmetric architecture with matched flow and compression on both sides, the present study removes positive electrode interference and enables a clean comparison of four electrode configurations: both heated (BH), positive not heated (PNH), negative not heated (NNH), and both not heated (BNH). This design permits a direct assessment of how single-sided modification introduces performance mismatch and masks true limitations when judged only by net polarization.

The V^{2+}/V^{3+} couple is generally recognized as the kinetically slower side of the VRFB, with significantly lower exchange current densities compared with the VO^{2+}/VO_2^+ redox couple [3]. Even though the V^{2+}/V^{3+} redox couple is commonly treated as a single redox couple, the two directions are not kinetically equivalent to not-heated electrodes, and this asymmetry can dominate cell behavior [4]. Its slow charge transfer often makes the negative electrode the limiting factor for power density and overall efficiency [5]. Therefore, a fundamental understanding of how electrode properties influence this half-reaction is essential, not only for identifying rate-determining processes but also for guiding the rational design of electrode modification strategies.

As shown in Chapter 3, heat treatment of carbon paper electrodes modifies morphology,

surface chemistry, wettability, and porosity. These changes are expected to directly influence the effective electrochemical surface area, the charge transfer kinetics, and the mass transport processes occurring within the porous electrode structure [6–8]. Heat treatment is known to enhance the reaction kinetics, but the extent to which it differentially benefits V^{3+} reduction reaction versus V^{2+} oxidation reaction, and how those kinetic gains interact with finite-rate transport in the porous electrode, has not been systematically resolved at the cell level. In particular, the interplay among charge transfer resistance, mass transport, ohmic resistance, and how these contributions evolve with applied current, remains insufficiently clarified [9].

The objectives of this chapter are as follows: (1) Quantify the effects of electrode heat treatment on the charge transfer and mass transport behaviors of the V^{2+}/V^{3+} redox couple, using both impedance spectroscopy and Tafel analysis to provide complementary perspectives on reaction kinetics. (2) Assess how these kinetic enhancements interact with mass transport limitations and ohmic losses to determine overall cell performance. By systematically comparing not-heated and heat-treated electrodes under symmetric cell operation, the chapter establishes the mechanistic basis for understanding performance differences and provides a framework for interpreting the positive half reaction analysis in Chapter 5.

4.2 Overall electrochemical performance

The overall electrochemical performance of the V^{2+}/V^{3+} symmetric cells under different electrode treatment conditions is first illustrated by polarization (I-V) curves.

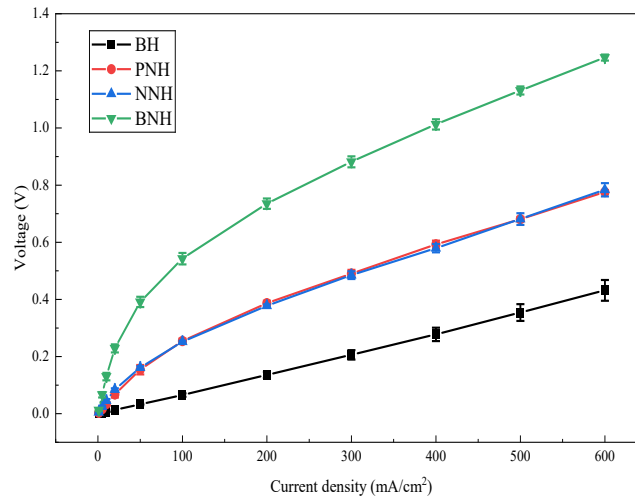


Fig. 4-1 I-V polarization curves

As shown in Figure 4-1, the total overpotential increases monotonically with current density for all configurations, but the relative magnitude follows a consistent order: $BNH > NNH \approx PNH > BH$. The BH condition cell displays the lowest and most linear voltage rise to 0.6 A/cm^2 , indicating that activation losses are strongly suppressed and transport remains manageable. By contrast, the BNH condition cell exhibits the steepest increase and the earliest deviation from linearity, reflecting severe kinetic and transport limitations. The single-sided cases (PNH and NNH) fall in between, though their total overpotentials are almost indistinguishable within the test range, this similarity should be further examined to clarify whether it results from a mutual compensation effect of different overpotentials rather than true equivalence.

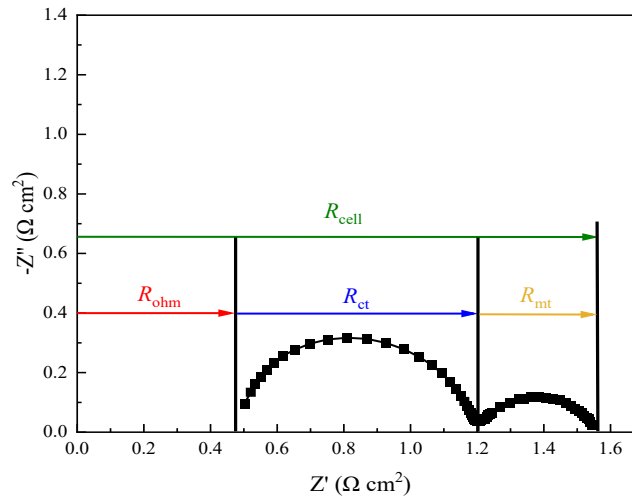


Fig. 4-2 EIS data fitting: Nyquist plot decomposition

EIS was then employed to deconvolute the contributions of charge transfer, mass transport, and ohmic resistances. A representative Nyquist plot with its equivalent circuit assignment is provided in Fig. 4-2, where the high frequency intercept corresponds to the ohmic resistance R_{ohm} , the diameter of the mid frequency semicircle represents the charge transfer resistance R_{ct} , and the diameter of the low frequency semicircle reflects finite mass transport resistance R_{mt} . This framework is applied consistently across all subsequent analyses to quantify how each resistance evolves with electrode treatment and applied current.

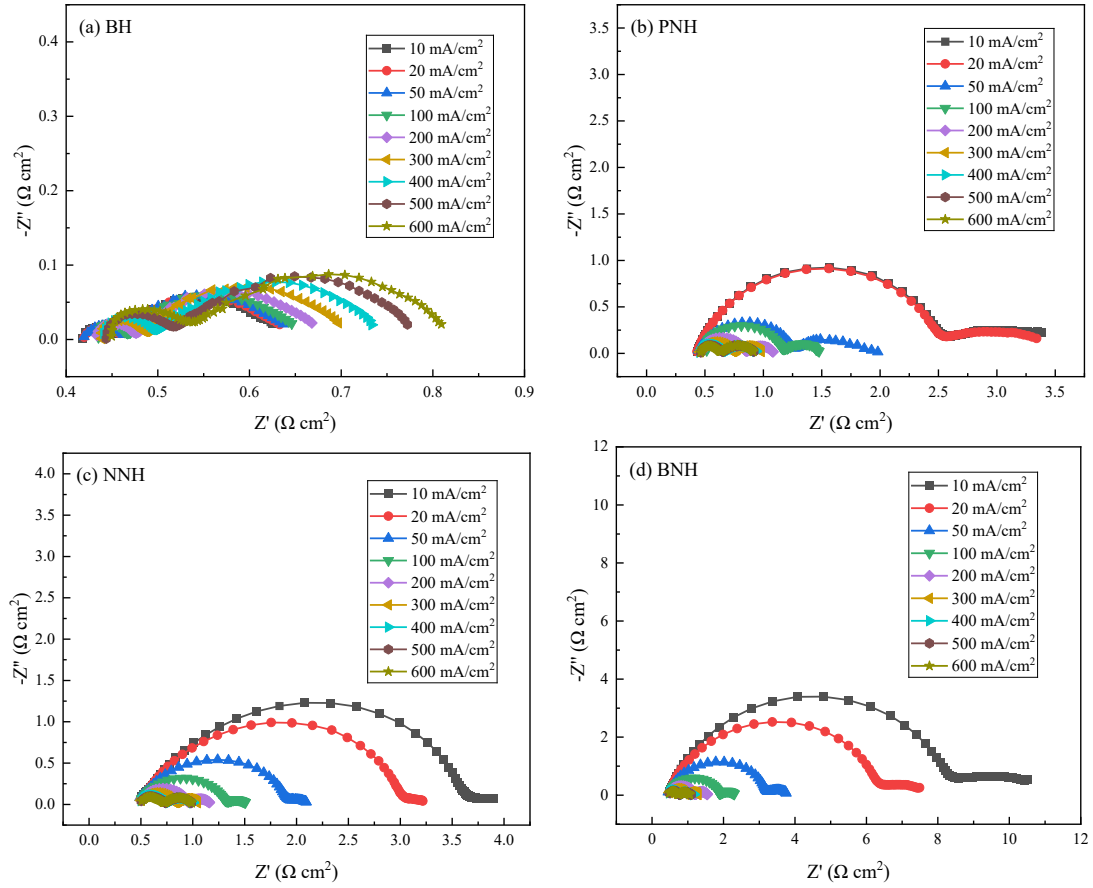


Fig. 4-3 Nyquist plots with applied DC currents (a) BH (b) PNH (c) NNH (d) BNH

Fig. 4-3 compares Nyquist plots of the four electrode configurations at OCV and under increasing current densities. In the BH case, the semicircle is strongly suppressed across the entire current range, indicating that charge transfer resistance is no longer the dominant loss mechanism. Instead, the low frequency semicircle associated with mass transport becomes more evident at high current densities. By contrast, in the BNH configuration, semicircles expand and distort significantly, reflecting the persistent slow kinetics of not-heated carbon and the growing contribution of mass transport. The two single-sided cases (PNH and NNH) both exhibit large charge transfer resistance, but their spectral shapes differ: PNH shows a bigger low frequency semicircle of mass transport limitations, while NNH displays relatively small mass transport resistance and remains dominated by charge transfer processes. This distinction implies that, although their I-V curves appear comparable, the underlying limitations differ fundamentally

depending on which electrode is not heat treated.

Comparative impedance behavior highlights two mechanistic insights. First, heat treatment effectively suppresses charge transfer overpotential by enlarging the ECSA and introducing oxygen functional groups that promote redox kinetics [6]. Once these activation barriers are mitigated, mass transport resistance emerges as the primary limitation, particularly under high current densities in the BH configuration. Second, stable operation across the full current range requires both electrodes to be treated and single-sided treatment not only introduces severe performance mismatch but also makes it difficult to identify the fundamentally different overpotential limiting factors. In particular, the apparent equivalence between PNH and NNH in terms of total polarization masks distinct origins of overpotential, with PNH exhibiting stronger mass transport limitations while NNH remains dominated by sluggish charge transfer. These observations underscore the need for impedance separation, motivating the quantitative extraction of charge transfer, mass transport, and ohmic contributions in the following discussion.

4.3 Decomposition of overpotentials

As described in Section 2.5.3, the total polarization loss of the symmetric cells is separated into charge transfer, mass transport, and ohmic contributions by fitting impedance spectra with a simplified equivalent circuit model and numerically integrating the resulting resistances. To ensure that this decomposition provides a faithful representation of the real cell behavior, the EIS-derived total resistance is cross-validated against the differential resistance extracted directly from measured polarization curves. The agreement between the two methods was quantified using the normalized root mean square error (NRMSE). The NRMSE was calculated as follows:

$$\text{NRMSE} = \frac{\sqrt{\frac{1}{n} \sum_{i=1}^n (R_{\text{EIS},i} - R_{\text{IV},i})^2}}{R_{\text{IV},\text{max}} - R_{\text{IV},\text{min}}} \quad (4-1)$$

where n is the number of current density conditions.

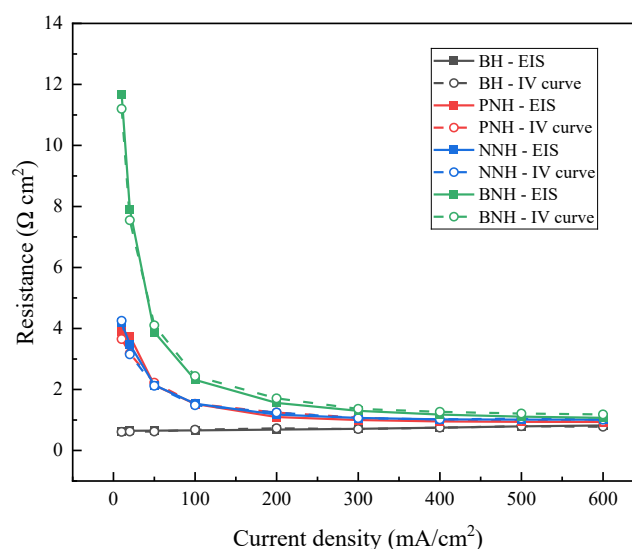


Fig. 4-4 Comparison of calculated total resistance derived from EIS and I-V curves

Fig. 4-4 compares the two approaches across the full current density range. The agreement is excellent with an NRMSE of 1.58%. This close correspondence confirms that impedance-based fitting captures the essential electrochemical processes without over-parameterization and can be reliably used to reconstruct overpotentials.

Building on this validated framework, the current-dependent resistance components are integrated to yield three distinct overpotential contributions: charge transfer, mass transport, and ohmic overpotential as described in Eq. (2-9). The sum of these three terms reproduces the measured polarization curves with high accuracy, indicating that the simplified representation adequately describes the physical origins of voltage loss in the V^{2+}/V^{3+} symmetric cells.

The following subsections examine each contribution in turn. Section 4.3.1 focuses on charge transfer overpotential, highlighting the impact of heat treatment on effective ECSA, standard rate constant, and apparent transfer coefficient. Section 4.3.2 then evaluates the emergence of mass transport limitations, especially at high current. Section 4.3.3 addresses the ohmic resistance and its dependence on electrode treatment. Together, this decomposition provides a mechanistic basis for interpreting how electrode modification changes which of the charge transfer, mass transport, or ohmic overpotentials dominates the performance.

4.3.1 Charge transfer overpotential

Fig. 4-5 presents Nyquist plots from EIS tests at OCV, while those under applied DC current are shown in Fig. 4-3. To eliminate the influence of the ohmic intercept and to better resolve the dynamic semicircle, R_{ohm} was subtracted so that the high frequency real part of impedance was set to zero. The charge transfer resistance R_{ct} under the four conditions follows the order: $BNH > NNH > PNH > BH$, indicating that the electrochemical reaction rates of V^{2+} and V^{3+} differed depending on whether the electrodes had undergone the heat treatment process.

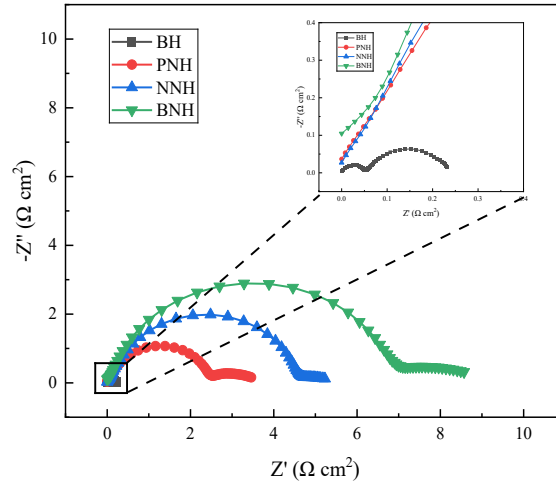


Fig. 4-5 Effect of heat treatment on EIS at OCV

As described in Section 2.5.5, based on the equivalent double layer capacitance C_{eff} , effective ECSA (A_{eff}) and reaction rate constant k_0 could be calculated. Table 4-1 shows the calculated normalized A_{eff} , obtained by dividing the effective surface area by the geometric active area, along with the kinetic rate constant k_0 .

Table 4-1 Effective electrode area and reaction rate constant

Heat treatment condition	Normalized A_{eff}	$k_0 / 10^{-5} \text{ cm s}^{-1}$
BH	73.36 ± 10.93	8.32 ± 2.33
PNH	11.38 ± 0.95	1.34 ± 0.23
NNH	11.77 ± 1.78	0.60 ± 0.08
BNH	9.26 ± 0.39	0.47 ± 0.15

For the normalized A_{eff} , the BH condition exhibits the highest value of 73.36, which is 7.9 times that of the BNH condition. Specifically, the partial removal of binder (see Fig. 3-1) exposes more of the porous carbon fiber structure, increasing the porosity and helping to eliminate air pockets between the electrolyte and the carbon surface (as described by the Cassie-Baxter effect [10]). The porosity is estimated using the ratio of pore volume to total volume, showing an increase from 0.857 ± 0.006 to 0.886 ± 0.003 after heat treatment (details are provided in the Supporting Information). In addition, the high temperature treatment creates pits on the fiber surface, thereby increasing surface roughness. According to the Wenzel equation [11], this enhanced roughness reduces the contact angle and further improves wettability (see Fig. 3-6), ultimately enhancing the ECSA. Meanwhile, an approximate 5 times increase is observed in oxygen functional groups (XPS results, see Section 3.3.2), similar to the value reported in [8], this modest increase in surface active oxygen contributes to improved wettability [12]. Furthermore, the presence of oxygen functional groups may directly serve as reaction sites, further increasing the ECSA [7].

The A_{eff} values under the PNH and NNH conditions are very close, indicating that heat treatment alters the physical properties of the electrodes without introducing selectivity differences for V^{2+} and V^{3+} ions. Moreover, the A_{eff} values under single-sided heated conditions only increase by approximately 25% compared to the BNH condition, which is significantly less than the increase observed in the BH condition. This suggests that, under single-sided heating, the growth in physically available surface area does not translate into fully utilized effective

surface area. This is because the reactions must match with ions on the opposite side, limiting the utilization of the additional available surface area.

For the reaction rate constant k_0 , the BH condition achieves the highest value of 8.32×10^{-5} cm/s, which was 17.7 times that of the BNH condition. It is generally accepted that the formation of oxygen functional groups during heat treatment plays a crucial role in the increase of k_0 for the V^{2+}/V^{3+} couple [7]. Notably, the k_0 value under the PNH condition is approximately double that under the NNH condition, indicating that heat treatment affected V^{2+} and V^{3+} reactions differently. The V^{3+} reduction reaction on the heat-treated NE side (PNH condition) is faster than the V^{2+} oxidation reaction on the heat-treated PE side (NNH condition). This indicates that heat treatment on the NE side enhanced V^{3+} reduction more effectively than it enhanced V^{2+} oxidation on the PE side. Furthermore, the k_0 value under the NNH condition is close to that of the BNH condition, suggesting that the V^{3+} reduction reaction on the untreated NE side is much slower, limiting the overall reaction rate of the system. Although the heat treatment on the PE side improves the V^{2+} oxidation reaction, it does not significantly increase k_0 , further highlighting the dominant role of V^{3+} reduction in system performance.

To further probe the charge transfer kinetics, the Tafel extrapolation is performed on the polarization curves as described in Section 2.5.4. Fig. 4-6 shows the Tafel fitting plots.

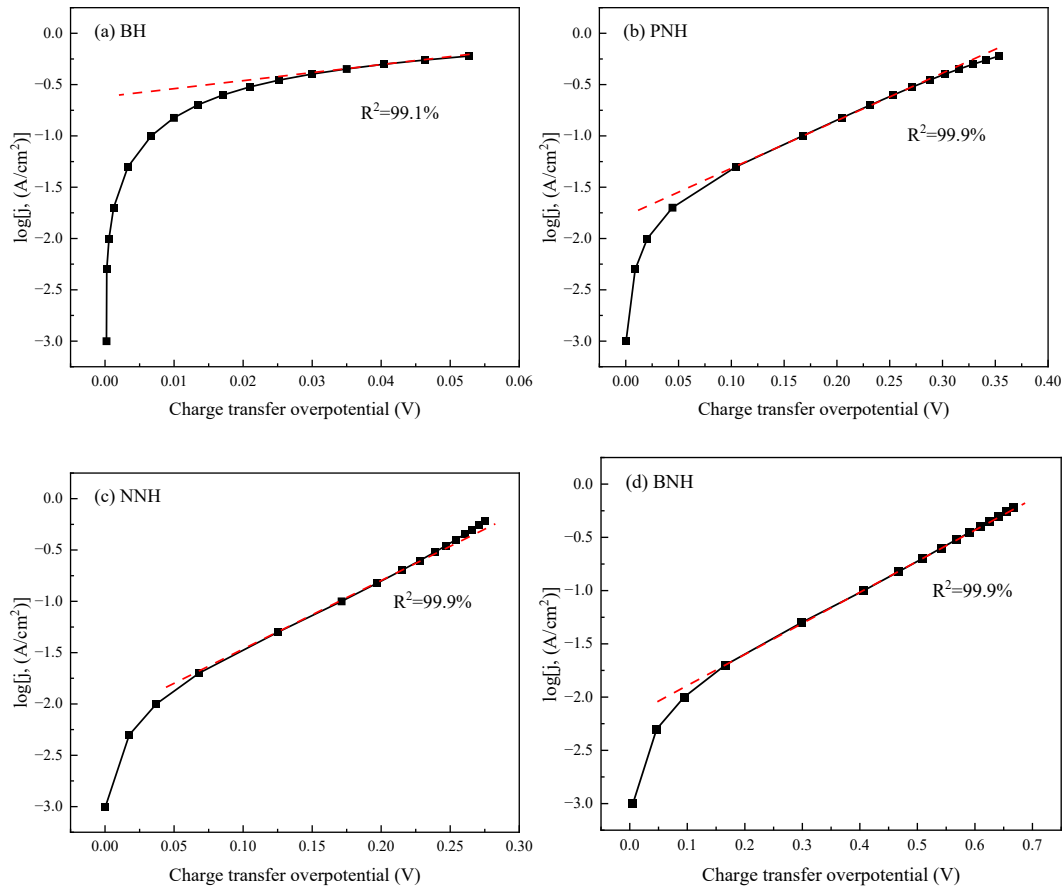


Fig. 4-6 Tafel fitting plots

Table 4-2 Tafel slope and charge transfer coefficient

Heat treatment condition	b (mV/dec)	Apparent α
BH	125.22±5.53	0.47±0.02
PNH	193.73±18.85	0.31±0.03
NNH	169.42±19.26	0.35±0.04
BNH	348.68±10.88	0.17±0.01

As shown in Table 4-2, the BH condition exhibits the highest α value of 0.47, approaching the commonly assumed value of 0.5, suggesting that the energy barriers for forward and reverse reactions are nearly symmetric. In contrast, the BNH condition yields a significantly lower α of 0.17, close to the value 0.15 reported in [1], indicating a highly asymmetric charge transfer process. It is generally accepted that α is influenced by three key steps at the electrode-

electrolyte interface: ion adsorption, electron transfer, and ion desorption [13]. Before heat treatment, the carbon paper surface lacks functional groups, offers limited active sites, and exhibits poor wettability. These factors can result in asymmetric energy barriers between oxidation and reduction reactions. Moreover, V^{2+} and V^{3+} ions differ in their adsorption and desorption behaviors on the carbon surface [4], which may lead to a deviation from the ideal case where the sum of anodic and cathodic α values is 1. Heat treatment introduces oxygen functional groups (e.g., C-O, C=O), improves wettability, and increases the density of active sites, all of which facilitate more uniform adsorption and desorption processes [14]. As a result, the reaction becomes more reversible and symmetric, with α values closer to 0.5 and a total α sum approaching 1.

Under the PNH and NNH conditions, α values are 0.31 and 0.35, respectively. This difference can be attributed to the distinct roles of V^{3+} in each half-cell. According to density functional theory calculations [4], the adsorption energies of V^{2+} and V^{3+} on a pristine graphite surface are -30.1 kcal/mol and -44.7 kcal/mol, respectively. This stronger binding may lead to slow desorption of V^{3+} when it is produced as the oxidation product on the PE side, thereby worsening reaction asymmetry and resulting in a lower apparent α . However, it must be recognized that the actual adsorption and desorption behavior in the electrolyte can be significantly influenced by the concentrations of vanadium and sulfate ions, the electrode material, surface morphology, and pretreatment processes [15]. Therefore, the interpretation of the observed α values should be considered on a case-by-case basis. It is important to note that, because a three-electrode system was not used, the obtained data reflects the integrated apparent kinetic parameters of the overall cell rather than the independent anodic or cathodic kinetics.

To further evaluate the consistency of kinetic parameters obtained by different approaches, the exchange current densities i_0 derived from Tafel analysis are compared with those calculated from EIS data. The results are summarized in Table 4-3:

Table 4-3 Exchange current density i_0 comparison of Tafel analysis and EIS calculation

Heat treatment condition	$i_0 / (\text{A}/\text{cm}^2)$ (Tafel)	$i_0 / (\text{A}/\text{cm}^2)$ (EIS)
BH	0.50 ± 0.16	0.47 ± 0.10
PNH	0.013 ± 0.0024	0.012 ± 0.0016
NNH	0.0058 ± 0.0012	0.0056 ± 0.00019
BNH	0.0036 ± 0.0012	0.0031 ± 0.0010

Although the two methods give similar values, there are also differences that can be attributed to the distinct measurement conditions. EIS is conducted at or near open-circuit voltage using small perturbations, whereas Tafel extrapolation relies on data collected at relatively high current densities under steady-state operation. These differing operational conditions inherently lead to discrepancies in the apparent kinetic parameters obtained by each method. In addition, the charge transfer overpotentials derived from EIS are used as input for the Tafel analysis; although efforts are made to clearly separate charge transfer and mass transport contributions, such separation remains challenging and may further contribute to quantitative differences.

Despite these numerical discrepancies, both methods yield consistent relative trends across the four experimental conditions. Moreover, EIS uniquely provides separate estimates of the effective surface area and intrinsic kinetic rate constant (A_{eff} and k_0), information that Tafel analysis alone cannot offer. In this sense, the two approaches are complementary: EIS supplies a detailed decomposition of resistive components and geometric effects, while Tafel analysis confirms the overall kinetic behavior under operating currents. Their combined use therefore provides a more comprehensive and reliable picture of the electrode reaction kinetics than either method on its own.

The charge transfer overpotential calculated from the R_{ct} obtained by EIS separation is shown in Fig. 4-7.

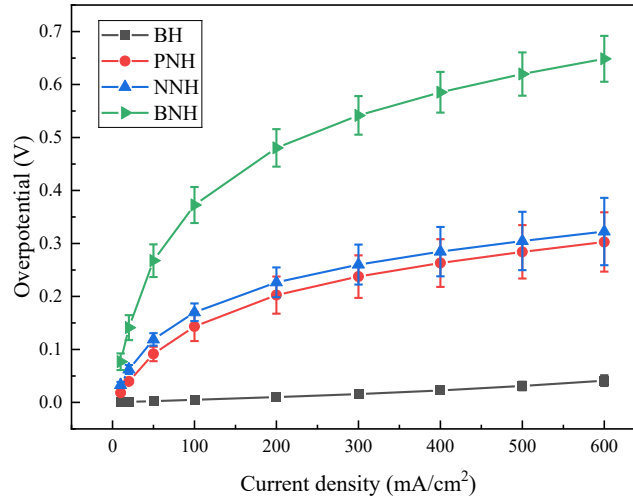


Fig.4-7 Charge transfer overpotential calculated from the equivalent circuit

As shown in Fig. 4-7, the relative magnitudes of charge transfer overpotentials under all current densities follow the order $BNH > NNH > PNH > BH$, consistent with the k_0 values calculated in Table 4-1. Although the A_{eff} and k_0 values for NNH and BNH are similar, the charge transfer overpotential is nevertheless significantly lower in the NNH condition. This discrepancy can be attributed to the difference in the charge transfer coefficient α which is 0.35 for NNH and 0.17 for BNH condition. According to the Tafel relationship:

$$\eta = \frac{RT}{\alpha n F} \ln \left(\frac{i}{i_0} \right) \quad (4-2)$$

where i is the current density, A/cm²; i_0 is the exchange current density, A/cm².

It could be found that a smaller α increases the slope, thereby amplifying the charge transfer overpotential, even when i_0 values (which were derived by A_{eff} and k_0) were similar. Consequently, BNH condition, with the smallest α (0.17), exhibits the largest charge transfer overpotential despite its similar A_{eff} and k_0 values to the NNH condition.

A similar trend is observed when comparing the PNH and NNH condition. Although the k_0 of PNH condition is approximately twice that of NNH condition, the charge transfer overpotential is slightly higher. This again highlights the role of α : PNH has a lower α (0.31) than NNH (0.35), which increases its Tafel slope and largely offsets the advantage of having a higher

k_0 . Moreover, at high current densities, the logarithmic nature of the Tafel equation reduces the sensitivity to i_0 , making α an important factor in determining the charge transfer overpotential.

Theoretically, as current density increases, R_{ct} is expected to gradually decrease, resulting in a slower growth rate of charge transfer overpotential [16]. However, under the BH condition, the growth rate of charge transfer overpotential slightly increases with current density, which differs from the other three conditions. This difference can be attributed to the high k_0 under the BH condition, leading to a much smaller charge transfer overpotential, where mass transport begins to dominate at high current densities. Insufficient reactant diffusion to the electrode surface lowers the surface reactant concentration, indirectly increasing R_{ct} [17]. In contrast, for the other three conditions, the lack of heat treatment results in large charge transfer overpotentials that remain dominant across all current densities. Under these conditions, the system operates under kinetic control, and mass transport limitations do not significantly affect the charge transfer overpotential, aligning with theoretical predictions.

These results demonstrate that heat treatment significantly improves the effective surface area A_{eff} , the reaction rate constant k_0 and the charge transfer coefficient α . However, this advantage is maximized only when both electrodes are heat-treated. Both-electrode heat treatment ensures optimal matching between the two electrodes, allowing both sides to fully utilize their enhanced surface properties and reaction kinetics. In contrast, single-sided heat treatment introduces a mismatch, with the untreated side severely limiting the overall system performance. Without heat treatment, the reduction reaction of V^{3+} to V^{2+} is much slower than the oxidation reaction of V^{2+} to V^{3+} . After heat treatment, this trend is reversed, with V^{3+} to V^{2+} exhibiting a faster reaction rate. This reversal can be attributed to the formation of oxygen functional groups during heat treatment, which selectively enhances the kinetics of V^{3+} reduction.

4.3.2 Mass transport overpotential

In VRFB porous electrodes, mass transport is governed by the convection-diffusion transport through the wetted pore network. At 50% SOC in a symmetric cell, the bulk

concentrations of the electroactive ions are equal. Therefore, mass transport resistance is governed by the effective diffusivity D_{eff} and the effective diffusion layer thickness δ_{eff} [18]. The mass transport overpotential extracted from EIS is shown in Fig. 4-8.

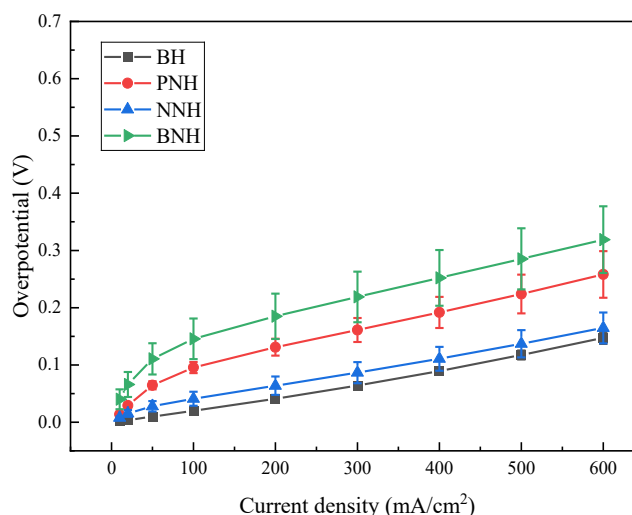


Fig.4-8 Mass transport overpotential calculated from the equivalent circuit

As shown in Fig. 4-8, the mass transport overpotential follows the order: BNH > PNH > NNH > BH. After heat treatment, the mass transport overpotential decreases significantly. For example, under the BH condition, the mass transport overpotential is reduced to 42% compared with BNH condition at 600 mA/cm². This reduction is attributed to partial thermal decomposition of the binder during heat treatment at 500 °C, which increases porosity and facilitates electrolyte transport. Simultaneously, heat treatment greatly improves the wettability of the electrode surface, increasing the effective ECSA and uniformly filling the electrode pores, thereby reducing local concentration gradients [19], which together increase D_{eff} and reduce δ_{eff} .

When the cell is single-sided heat treated, the mass transport overpotential under the PNH condition is significantly higher than that under the NNH condition. Under single-sided heat treatment conditions, both PNH and NNH consist of one not-heated and one heat-treated electrode under identical geometry and flow, so the mean of δ_{eff} across the two sides is expected to be comparable. Therefore, the observed difference in mass transport overpotential can be attributed

to the effective diffusion coefficient D_{eff} , which reflects the intrinsic ionic diffusivity and porous electrode structure, in particular the difference in the diffusion coefficients of V^{2+} and V^{3+} .

According to rotating disk electrode (RDE) studies reported in the literature [20], the diffusion coefficients determined via Levich analysis are $D_{V^{2+}} = 8.5 \times 10^{-12} \text{ m}^2/\text{s}$ and $D_{V^{3+}} = 2.1 \times 10^{-11} \text{ m}^2/\text{s}$, respectively. These intrinsic diffusion coefficients differ because V^{2+} and V^{3+} have different charges and correspondingly different hydration structures in sulfuric acid-based electrolytes, leading to different effective hydrodynamic diameter and mobilities. Consequently, under otherwise identical conditions, the lower diffusivity of V^{2+} ions results in greater concentration polarization and thus leads to a higher mass transport overpotential in the PNH configuration, where the positive electrode remains not heated, compared to the NNH configuration. This interpretation is also consistent with the impedance spectra: the PNH condition exhibits stronger low frequency semicircle than NNH, confirming that the not-heated side becomes the dominant transport resistance.

4.3.3 Ohmic overpotential

The ohmic overpotentials under different conditions calculated by integration of individual resistances from the equivalent circuit are shown in Fig. 4-9, which is composed of electrolyte resistance, membrane resistance, and contact resistance.

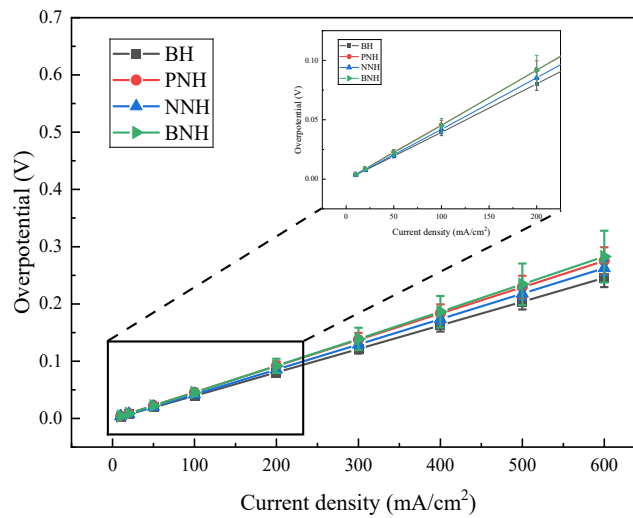


Fig. 4-9 Ohmic overpotential calculated from the equivalent circuit

Fig. 4-9 shows that the ohmic resistance remains nearly constant with increasing applied DC current density. The average ohmic resistance across all conditions is $0.44 \pm 0.025 \Omega \text{ cm}^2$, resulting in a linear relationship between the ohmic overpotential and the applied current density. The ohmic overpotentials for the PNH, NNH, and BNH conditions are very similar, slightly higher than the BH condition.

To further understand the contributions to total ohmic resistance, the role of membrane resistance is analyzed. According to [21], the ionic conductivity of Nafion 117 in 1.75 mol/L vanadium sulfate and 5 mol/L sulfuric acid solution was 0.034 S/cm. Assuming similar conductivities for Nafion 211, the estimated membrane resistance was $0.0735 \Omega \cdot \text{cm}^2$, accounting for 16.7% of the total resistance, which is lower than the 40% reported in the literature [7]. This lower contribution is likely due to the thinner 25 μm Nafion 211 membrane used in this study.

Since electrode resistances are primarily electronic and typically an order of magnitude lower than ionic resistance [22], the ionic resistance of the electrolyte within the porous electrode dominates the total ohmic resistance. According to Refs. [23,24], the effective bulk ionic conductivity (κ_{bulk}) of a 1.5 M vanadium + 4.0 M H_2SO_4 electrolyte is 297 mS/cm. Using the Bruggeman method [24], the effective ionic conductivity is estimated to be approximately 235.6 mS/cm for the not-heated electrode (porosity 0.857), whereas a value of 247.7 mS/cm is obtained for the heat-treated electrode (porosity 0.886). Based on an average effective ionic conductivity of 240 mS/cm and a thickness of 800 μm for the two compressed electrodes, the ionic resistance of the electrolyte-filled porous electrode layer is estimated to be approximately $0.333 \Omega \cdot \text{cm}^2$, accounting for 75.8% of the total ohmic resistance. Together with the membrane contribution of 16.7%, the remaining 7.5% is attributed to interfacial contact resistance.

This modest increase in κ_{eff} indicates that the partial removal of binder during heat treatment leads to a slight porosity enhancement, which only slightly improves the ionic conductivity. Moreover, due to the short heating duration, binder removal was incomplete, and the porosity improvement remains limited. Consequently, only minor changes in the ohmic

overpotential are observed from Fig. 4-9. It is also important to note that if the wettability between the electrode and the electrolyte is poor, the electrolyte may not fully infiltrate the porous structure, potentially forming gas pockets and reducing the effective ionic conduction pathways, thereby increasing the ohmic resistance despite the high inherent conductivity of the electrolyte.

4.3.4 Overall overpotential decomposition

To better understand the sources of these differences, the contributions of ohmic, charge transfer, and mass transport overpotentials are analyzed using EIS, as shown in Fig. 4-10.

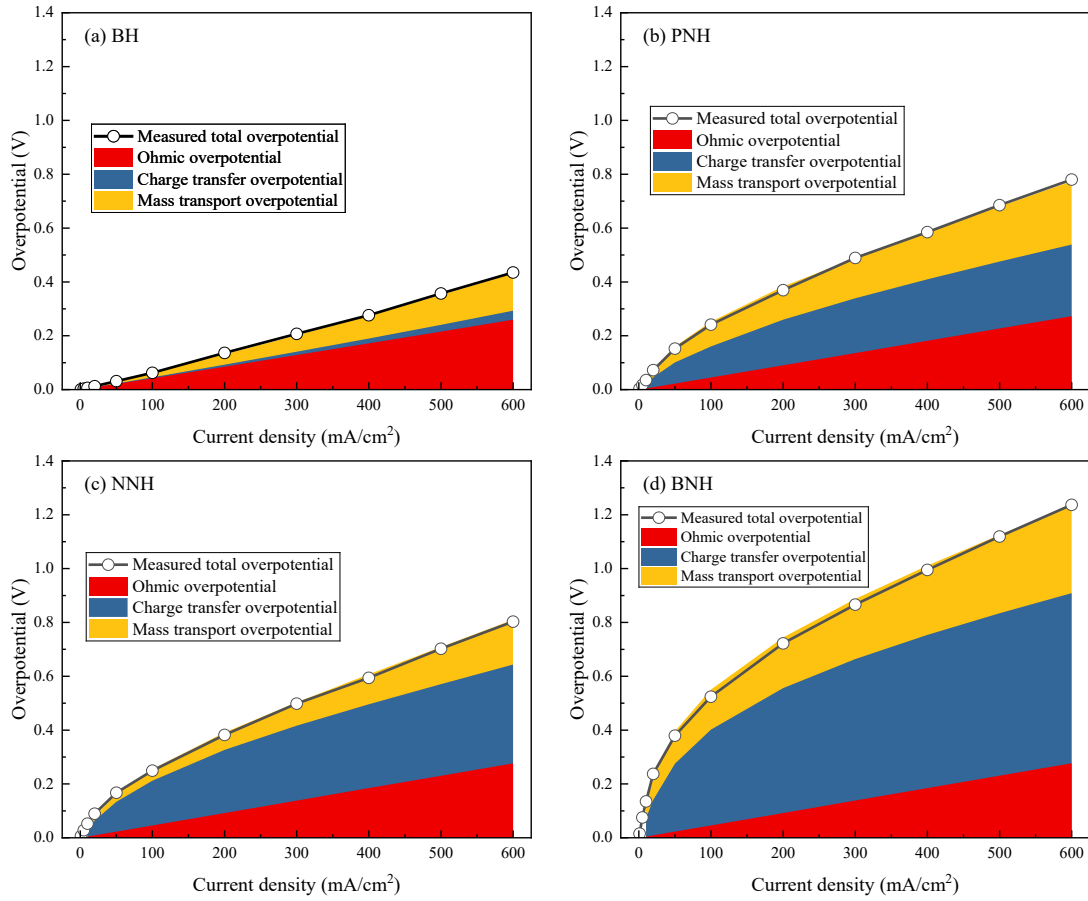


Fig. 4-10 Results of overpotential decomposition analysis

Fig. 4-10 illustrates the contributions of ohmic, charge transfer, and mass transport overpotentials to the total overpotential under each condition. The comparison between directly measured overpotentials and those reconstructed from EIS fitting yields an NRMSE of 0.85%,

indicating that each overpotential is accurately decomposed.

For the BH condition, ohmic overpotentials dominate, while charge transfer overpotentials are minimal. This is because heat treatment significantly reduces charge transfer resistance with only minor effects on ohmic resistance. The linearity of the I-V curve across current densities further supports the dominance of ohmic resistance under this condition. For the PNH condition, the apparent reaction rate of V^{2+} on the untreated PE side is significantly reduced due to the absence of heat treatment. At the same time, V^{2+} has a smaller diffusion coefficient than V^{3+} , which enhances the mass transport limitation on the PE side. As a result, ohmic, charge transfer, and mass transport overpotentials become comparable in magnitude and contribute similarly to the total overpotential. In contrast, for the NNH condition, although the total overpotential is similar to that under the PNH condition, charge transfer overpotentials dominate. This is because the V^{3+} reaction on the not-heated NE side exhibits a much lower apparent kinetic rate constant than the V^{2+} reaction on the heat-treated PE side, while the larger diffusion coefficient of V^{3+} compared to V^{2+} alleviates mass transport limitations and keeps the mass transport overpotentials relatively small. Finally, for the BNH condition, both charge transfer and mass transport overpotentials increase significantly, with charge transfer overpotential being the dominant factor. This stands in sharp contrast to the BH condition, where charge transfer overpotential is minimal, highlighting the significant improvement in electrochemical reaction kinetics due to heat treatment.

Notably, the near equivalence in overall overpotentials observed for the PNH and NNH conditions underscores the importance of separating the individual contributions from charge transfer and mass transport processes. Although the net overpotentials appear similar, the underlying mechanisms differ markedly: in the PNH condition, a lower charge transfer overpotential is offset by a higher mass transport overpotential, while in the NNH condition, a higher charge transfer overpotential is accompanied by lower mass transport resistance. This compensatory behavior suggests that the overall cell performance, when evaluated solely by net

overpotential, may mask significant differences in the electrochemical kinetics and transport phenomena. Therefore, a more detailed analysis of these individual contributions is essential for understanding and optimizing electrode performance in such systems.

On this basis, the impact of heat treatment on the distribution of overpotentials across the four conditions can be summarized as follows. Under the BH condition, charge transfer overpotential contributes the least. For the PNH condition, the contributions of the three overpotentials are comparable. For the NNH and BNH conditions, the charge transfer overpotential contribution is the highest due to the low reaction rate of V^{3+} on the not-heated NE side. This comparison highlights that while the BH condition achieves the lowest charge transfer overpotential, single-sided heat treatment introduces a mismatch, with the untreated side limiting overall performance.

Overall, the decomposition analysis confirms that heat treatment fundamentally changes the balance of overpotentials, shifting the primary limitation from charge transfer to mass transport or ohmic pathways depending on configuration.

4.4 Conclusions

This chapter systematically analyzes the electrochemical behavior of the V^{2+}/V^{3+} couple using symmetric cell configurations, enabling clear separation of charge transfer, mass transport, and ohmic contributions. A straightforward method for separating impedance contributions is introduced using EIS, validating excellent agreement with I-V results. These findings contribute to a deeper understanding of the redox processes in VRFBs.

(1) The intrinsic reaction rate constants k_0 of V^{2+} and V^{3+} ions are not identical, with V^{3+} reduction exhibiting lower kinetics compared to V^{2+} oxidation under the same conditions. This differs from the traditional assumption of uniform reaction kinetics within the redox couple and suggests the need to treat the two ions individually in performance analysis.

(2) The diffusion coefficients of V^{2+} and V^{3+} ions also differ significantly. Contrary to common assumptions, V^{3+} diffuses faster than V^{2+} under the concentrated electrolyte conditions

employed here. This discrepancy directly results in higher mass transport overpotentials when V^{2+} is the reacting species, consistent with EIS-derived trends.

(3) Heat treatment of carbon electrodes significantly enhances their performance by improving reaction kinetics, porosity, and wettability. However, the impact of heat treatment is not uniform: for reaction kinetics, V^{3+} reduction benefits more substantially than V^{2+} oxidation, reflecting selective improvements in catalytic activity. In contrast, for mass transport, V^{2+} shows greater benefits from heat treatment due to reduced local concentration gradients and enhanced diffusion within the porous structure. Furthermore, single-sided heat treatment introduces electrode mismatches, limiting overall system improvements and emphasizing the importance of uniform treatment for both electrodes.

The electrolyte used in this study contains 4.3 M sulfuric acid. Since the electrochemical behavior of vanadium species is sensitive to sulfuric acid concentration, the kinetic and mass transport responses observed here are influenced by the ionic strength, viscosity, and vanadium speciation at this acid concentration. These effects should be taken into account when extrapolating the present results to VRFB systems operated at different acid concentrations.

In conclusion, this study demonstrates that V^{2+} and V^{3+} ions exhibit intrinsic properties and respond differently to electrode modifications. The validated method for impedance separation provides a reliable approach for analyzing redox system electrochemical performance. Recognizing these differences is crucial for optimizing electrode design and electrolyte composition to further enhance the efficiency and performance of VRFB systems. These insights into the negative half reaction provide a benchmark for comparison with the positive side (VO^{2+}/VO_2^+), which will be discussed in Chapter 5.

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Chapter 5

Electrode Heat Treatment in Symmetric Cells: $\text{VO}^{2+}/\text{VO}_2^+$ Half Reaction

5.1 Introduction

This chapter investigates the kinetic and mass transport behaviors of the positive electrolyte half reaction ($\text{VO}^{2+}/\text{VO}_2^+$) in VRFBs using symmetric cells. As in Chapter 4, this approach isolates a single half-reaction under controlled conditions and avoids the coupling effects inherent in full cell tests. By eliminating the influence of the $\text{V}^{2+}/\text{V}^{3+}$ couple, the present study enables a more direct evaluation of intrinsic positive electrode behavior [1]. Operating at 50% SOC with matched flow rates and compression on both sides allows a clean comparison among both heated (BH), positive electrode not heated (PNH), negative electrode not heated (NNH), and both not heated (BNH) electrode configurations, thereby revealing how single-sided modification impacts stability and apparent performance.

Unlike the $\text{V}^{2+}/\text{V}^{3+}$ couple, the $\text{VO}^{2+}/\text{VO}_2^+$ reaction is generally regarded as kinetically faster, exhibiting smaller intrinsic activation losses at moderate current densities [2]. However, the positive half reaction is chemically more complex: speciation shifts and solid phase precipitation (e.g., V_2O_5 -like phases) can arise under high overpotentials or unfavorable local composition, coupling interfacial kinetics with transport and surface chemistry [3,4]. As defined in Section 2.2, “precipitation” in this thesis refers to vanadium oxo species and/or vanadyl-sulfate coordination formed on the carbon electrode surface during operation, as identified ex-situ by optical observation, SEM, and Raman spectroscopy. As a result, while the positive half reaction is not typically the rate-limiting side for power loads, it often governs stability and durability under practical high current operation [4].

Building on Chapter 3, heat treatment modifies morphology, porosity, and surface oxygen functional groups of the carbon paper, improving wettability and enlarging the effective ECSA [5]. For the $\text{VO}^{2+}/\text{VO}_2^+$ couple, however, the effect of heat treatment on reaction kinetics is far

less settled than for the V^{2+}/V^{3+} couple. While some studies report clear benefits in reducing charge transfer resistance and facilitating faster charge transfer kinetics, others argue that the kinetic gains are slight or inconsistent under practical operating conditions [6–8]. This divergence of opinion underscores the need for a systematic assessment of how electrode modification truly influences the positive half reaction kinetics.

At the same time, the VO^{2+}/VO_2^+ couple is prone to precipitation [9]. Chemical instability of VO_2^+ at high SOC can trigger speciation changes and the formation of V_2O_5 -like solids, which blocks the internal pores of porous electrodes and increases mass transport resistance [4]. These precipitation processes interact with interfacial kinetics but represent a distinct limitation, often dominating long term stability and durability at elevated current densities [10]. Consequently, the positive side presents a coupled problem: the intrinsic kinetics may or may not benefit from heat treatment, but stability is invariably constrained by precipitation-limited operation.

The objectives of this chapter are therefore as follows: First, to clarify how heat treatment influences the apparent charge transfer behavior of the VO^{2+}/VO_2^+ couple, thereby addressing the controversy surrounding its kinetic impact. Second, to determine how mass transport resistances and precipitation onset evolve under different electrode conditions. Third, to mechanistically link the precipitation threshold, which is defined as the onset current density identified from potential slope changes and low frequency impedance growth, with overpotential, interfacial kinetics, and irreversible resistance accumulation. By systematically comparing not-heated, heat-treated, and asymmetric configurations under symmetric cell operation, this chapter establishes a balanced framework for evaluating both the kinetic and stability aspects of the positive half reaction and prepares the ground for integrated discussion in Chapter 6.

5.2 Precipitation overpotential

5.2.1 Overall polarization curves

The overall electrochemical performance of the VO^{2+}/VO_2^+ symmetric cells under different electrode treatment conditions is first illustrated by I-V curves. For each configuration,

polarization measurements were independently repeated three times, and the representative curves shown here are consistent with the averaged behavior.

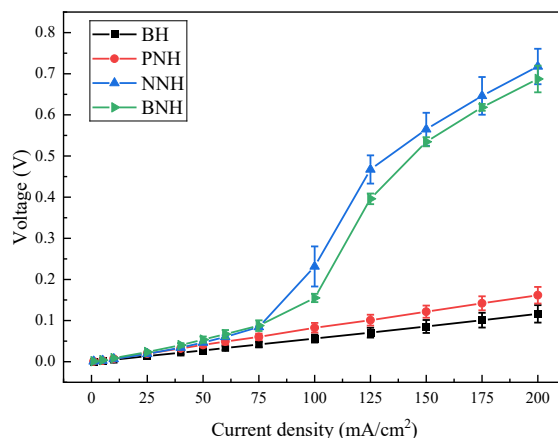
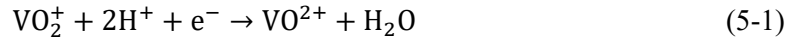


Fig. 5-1 I-V polarization curves

Fig. 5-1 shows the I-V characteristics of the symmetric VRFB cells equipped with four different electrode-treatment configurations. The BH cell always has the lowest polarization curve, rising almost linearly, confirming that both-electrode heat treatment simultaneously improves charge transfer kinetics and mass transport. The curve for the PNH is only slightly higher than BH, indicating that heat treatment of the negative electrode alone already provides most of the performance benefit, whereas heat treatment of the positive electrode alone is much less effective.

The NNH cell shows a similar trend to BH and PNH up to 75 mA/cm². However, when the current density reaches 100 mA/cm², the voltage rises sharply. For the BNH cell, the overpotential is the highest at low current densities (≤ 75 mA/cm²) and it increases slowly until a sharp rise appears at 125 mA/cm². This is similar to the NNH cell but happens at a lower current density. Neither BH nor PNH shows such a sudden increase. Since charge transfer, ohmic, and regular mass transport losses increase smoothly with current [11], these sudden jumps indicate there is an additional polarization mechanism that only appears when the negative electrode is not heat-treated. This highlights that modification of the negative electrode surface is more critical than that of the positive electrode for improving cell performance.

During the charging process, the VO_2^+ reduction reaction at NE is as follows:



Under high current density, the proton concentration near the NE surface can decrease due to proton consumption in the reduction reaction, leading to a local rise in pH [12]. This phenomenon can occur regardless of whether the electrode is heat-treated, but electrodes that are not heat treated typically exhibit poorer wettability and lower effective surface area, which tend to aggravate local pH elevation under the same operating conditions. It has been reported that an increase in pH can induce the deprotonation/hydrolysis of VO_2^+ [13], leading to the formation of vanadium oxo species and/or vanadyl-sulfate coordination precipitation. These possibilities motivate a closer examination of the impedance response under DC bias.

5.2.2 Nyquist analysis under DC bias

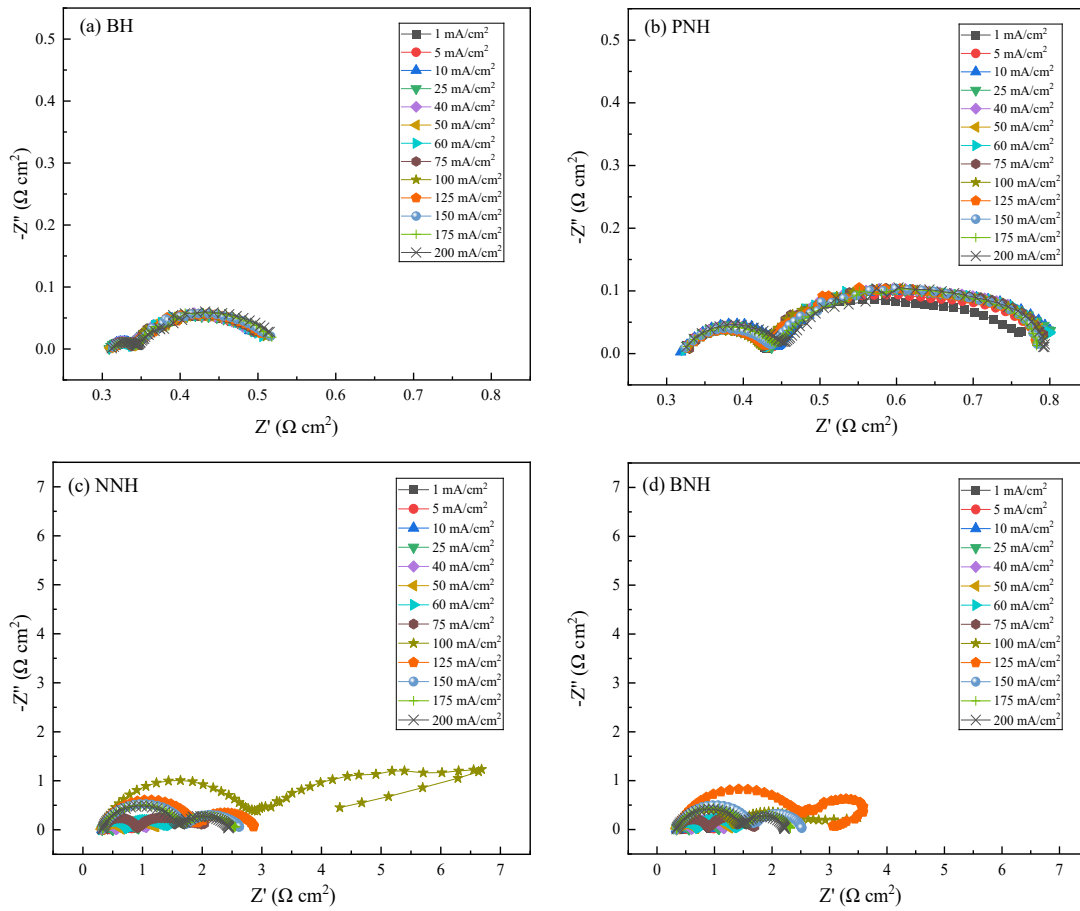


Fig. 5-2 Nyquist plots with applied DC currents (a) BH (b) PNH (c) NNH (d) BNH

As shown in Fig. 5-2 (a, b), the Nyquist plots for the BH and PNH conditions exhibit similar electrochemical behaviors. Although the overall impedance of the PNH condition is higher than that of BH, both conditions show a gradual and smooth variation of impedance with increasing DC current density. No abrupt impedance changes are observed within the entire measured range, as evidenced by the minimal difference between Nyquist plots at low (1 mA/cm^2) and high current densities (200 mA/cm^2). This behavior shows stable electrochemical interfaces without significant side reactions or precipitation under these conditions.

In contrast, Fig. 5-2 (c, d) shows markedly different behaviors for the NNH and BNH conditions. Both exhibit distinct impedance anomalies characterized by abrupt impedance increases at approximately 100 mA/cm^2 and 125 mA/cm^2 , respectively. The low frequency regions of the Nyquist plots feature abnormal backward-turning loops, indicative of significant interfacial changes. This phenomenon can be attributed to the formation of precipitation products, such as vanadium-oxo hydrates and vanadyl-sulfate hydrates (see Section 5.2.5 for the speciation scheme), leading to partial blockage of electrode pores and electrolyte pathways. The subsequent rapid decrease in impedance at higher current densities beyond this impedance peak is likely due to a combination of partial dissolution or redistribution of these precipitates and additional side reactions, making the Nyquist plots at higher currents insufficient to fully capture the total overpotential.

These observations highlight the critical role of electrode heat treatment in mitigating sudden impedance increases associated with precipitation, particularly on the negative side. They also suggest the possibility of localized pH shifts and solid formation when the negative electrode is not heat-treated, with consequential impacts on charge transfer and mass transport behavior. These abnormal phenomena raise the question of whether the assumptions of conventional EIS remain valid under such conditions, which will be discussed in the following section.

5.2.3 EIS limitation under precipitation

Conventional EIS assumes small perturbations, linearity, and a quasi-steady, time-

invariant operating point. When precipitation/gel complexes form and evolve in the order of minutes, the system departs from these assumptions: parameters drift during acquisition and the response is no longer strictly linear time invariant.

In measurements, precipitation/gel complex formation at the not-heated negative side develops on a minute timescale once the current density reaches 100-125 mA/cm². Because a single sweep extends to 0.01 Hz (100 s per point), the operating point drifts during acquisition, departing from the small perturbation, time invariant assumptions of conventional EIS. As a result, the spectra capture instantaneous increases in R_{ct} and R_{mt} , but the progressive blocking and any film/precipitation related barriers that are not explicitly parameterized in the simplified circuit are not fully assigned. Consistently, $\eta_{tot} \approx \eta_{EIS}$ when precipitation is absent (BH/PNH), whereas $\eta_{tot} > \eta_{EIS}$ when it occurs (NNH/BNH). Therefore, $\eta_{prc} = \eta_{tot} - \eta_{EIS}$ is defined as an operational residual summarizing this evolving contribution while retaining the conventional EIS components.

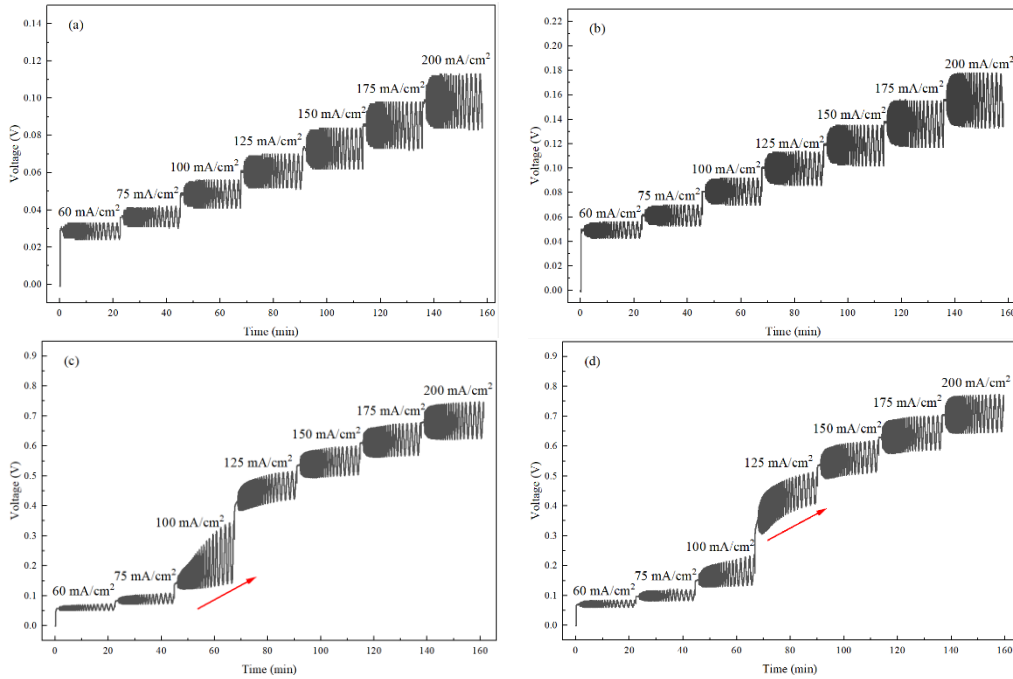


Fig. 5-3 Voltage drift during EIS experiment (a-d) BH, PNH, NNH and BNH conditions

Fig. 5-3 (a) and (b) (BH and PNH) show smooth and stable voltage traces even at high current densities, without step-like rises or drifts. This suggests that no detectable precipitation/gel complex occurs under these conditions, and the system remains close to steady state. Consistently, in these cases η_{tot} and η_{EIS} agree well, confirming that the EIS-based decomposition is reliable when precipitation is absent. By contrast, Fig. 5-3 (c) and (d) (NNH and BNH) exhibit clear non-stationary behavior once the current density exceeds 100-125 mA/cm². Step-like increases, drifts, and oscillations appear on a minute timescale, highlighted by the red arrows. This timescale is comparable with the low frequency domain of EIS, meaning that the operating point drifts significantly during a single frequency sweep, which explains why standard fitting underestimates the added polarization.

5.2.4 Quantification of precipitation overpotential

Using the procedure in Section 2.5.3, the total overpotential was reconstructed by summing the EIS-derived charge transfer, mass transport, and ohmic components. Then the precipitation residual η_{prc} was calculated as defined in Section 5.2.3.

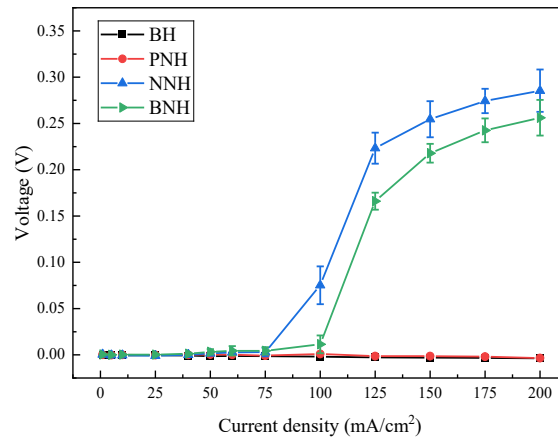


Fig. 5-4 Comparison of η_{prc}

Fig. 5-4 shows that the η_{prc} is almost 0 across the entire current range under BH and PNH conditions. This agreement demonstrates that the conventional EIS-based separation is accurate when no side reactions or additional polarization mechanisms are present. It is noted that slightly

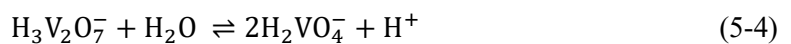
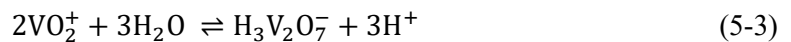
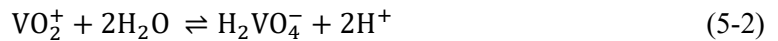
negative precipitation overpotentials may occur due to experimental or fitting errors and are not physically meaningful.

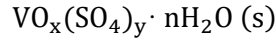
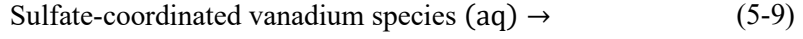
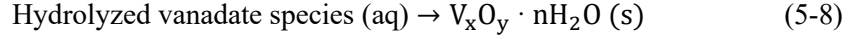
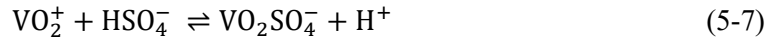
In contrast, in the NNH and BNH conditions, a significant difference arises between the reconstructed and measured total overpotential, especially at higher current densities. This deviation is attributed to the precipitation overpotential induced by precipitation-related losses, which is consistent with the emergence of an additional loss not represented by the equivalent circuit. Moreover, the current density at which η_{prc} begins to increase is consistent with the onset current of the instability observed in Fig. 5-3.

Therefore, in this study, η_{prc} serves as an operational metric that complements the classic EIS decomposition: it remains near zero when the system is steady and precipitation-free (BH/PNH), but rises measurably when additional, slowly evolving barriers develop (NNH/BNH). The physical origin of these barriers is examined next in the mechanistic analysis (Section 5.2.5) and verified by post-mortem microscopy and spectroscopy (Section 5.2.6).

5.2.5 Mechanistic clarification

To capture the proton-coupled reaction that accompanies VO_2^+ chemistry, a set of representative equilibria is summarized in Eq. (5-2) to Eq. (5-7), adapted from references [14,15]. These activity dependent acid-base/coordination reactions illustrate Le Chatelier self-buffering under local H^+ depletion and the pathway competition between hydrolysis and sulfate coordination. To reflect immobilization, two operational phase-transition arrows (not strictly balanced reactions) are introduced in Eq. (5-8) and Eq. (5-9) to denote condensation into hydrated solids:





Here, “vanadate” denotes hydrolyzed vanadium oxycomplexes. A quantitative speciation would require a full thermodynamic database (activity/ionic-strength dependent), which is beyond the present scope. The resulting condensed phases can block pores and impede ion/electron transport, introducing an additional precipitation overpotential η_{prc} , consistent with the sudden voltage jumps.

As shown in Fig. 5-4, η_{prc} emerges earlier and grows faster for NNH (100 mA/cm²) than for BNH (125 mA/cm²). During charging, the negative electrode (NE) supports VO_2^+ reduction (Eq. (5-1)), consuming two protons per electron. When the NE is not heat-treated (NNH and BNH), poorer wettability and smaller effective surface area hinder electrolyte renewal and local proton supply, promoting interfacial pH rise even at moderate currents. In NNH, the positive electrode is heat-treated while the NE remains not heat-treated. Thus, this asymmetry concentrates polarization at the NE, intensifying local proton depletion and increasing the hydrolysis/coordination thresholds (Eq. (5-2) to Eq. (5-7)), so that precipitation is triggered at a lower current (100 mA/cm²). In BNH, both electrodes are not heated, and the more uniformly poorer interfaces delay the localized triggering at the NE, shifting the onset to 125 mA/cm² and yielding a more gradual subsequent growth. Once precipitation starts, hydrolysis releases H^+ (Eq. (5-2) to Eq. (5-7)), which partially buffers further pH rise, thus, the increase of η_{prc} tends to become more gradual at higher currents.

These considerations provide a mechanistic basis for the precipitation overpotential and its dependence on electrode configuration, coherently linking proton-coupled speciation,

interfacial wettability/ECSA, and the observed non-steady onset. The physical evidence for these solids is presented next via post-mortem microscopy and spectroscopy (Section 5.2.6).

5.2.6 Morphological and spectroscopic verification

To obtain direct evidence for vanadium-oxide precipitation on the negative electrode, the cells were dismantled after the electrochemical and EIS experiments, and the electrodes were subjected to optical microscopy and Raman spectroscopy. Moreover, to further examine the solid phases associated with precipitation, post-mortem SEM-EDX analysis was later performed on separate vacuum-dried samples.

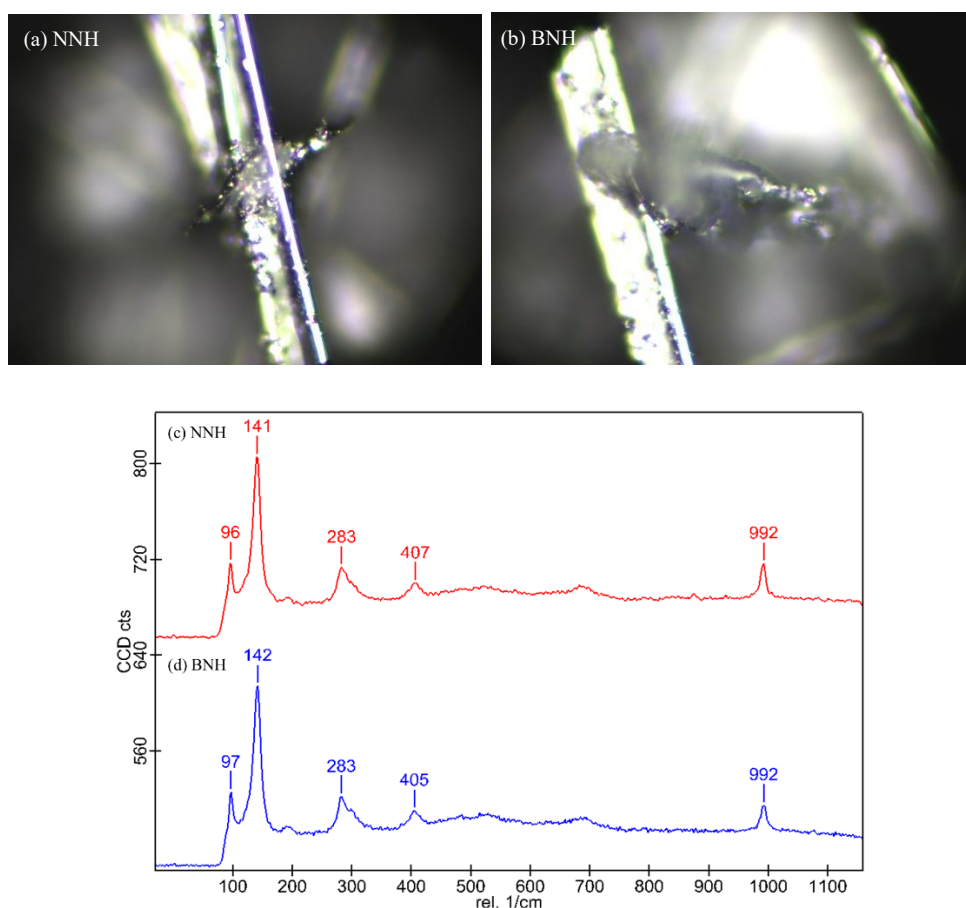


Fig. 5-5 Optical microscopy images (a, b) and Raman spectra (c, d) of precipitation formed on the NE under the NNH and BNH conditions

Fig. 5-5 (a, b) shows representative optical micrographs of the NE after electrochemical tests under the NNH and BNH conditions. The images reveal loosely attached and irregularly shaped precipitates distributed non-uniformly along the carbon fibers. Most of the observed material appears amorphous and gel-like, which is consistent with the expected formation of vanadium oxo species and/or vanadyl-sulfate precipitation during cycling [16]. In some regions, sharper and more faceted protrusions are also present; however, as similar morphologies can result from binder residues or other non-crystalline materials, optical microscopy alone is insufficient to determine their chemical identity or structural nature. The coexistence of these diverse morphological features suggests that precipitation at the electrode surface occurs under heterogeneous conditions and is not simple drying remains of the bulk electrolyte.

To further investigate the chemical nature of precipitation, Raman spectroscopy was conducted in regions visually identified as protrusions. As shown in Fig. 5-5 (c, d), the obtained Raman spectra exhibit distinct peaks around 96-97, 141-142, 283, 405-407, and 992 cm^{-1} . These bands resemble those commonly reported for vanadium oxo frameworks [17]. Specifically, the lowest-frequency peak at 96-97 cm^{-1} is associated with inter-layer shear vibrations, while the bands at 141-142 cm^{-1} , 283 cm^{-1} , and 405-407 cm^{-1} correspond to inter-layer bending, V-O-V bridging-oxygen bending, and symmetric V-O-V bending modes, respectively [18]. Most notably, a band near 992 cm^{-1} commonly assigned to the terminal V=O stretch appears together with these lattice modes, and sulfate-related bands (~ 984 and 1045 cm^{-1}) are not resolved at these locations, but this does not exclude sulfate coordination due to potential overlap or baseline effects [14]. Overall, this spectral pattern is consistent with vanadium oxo species (including hydrated and partially disordered domains), possibly with vanadyl-sulfate contributions.

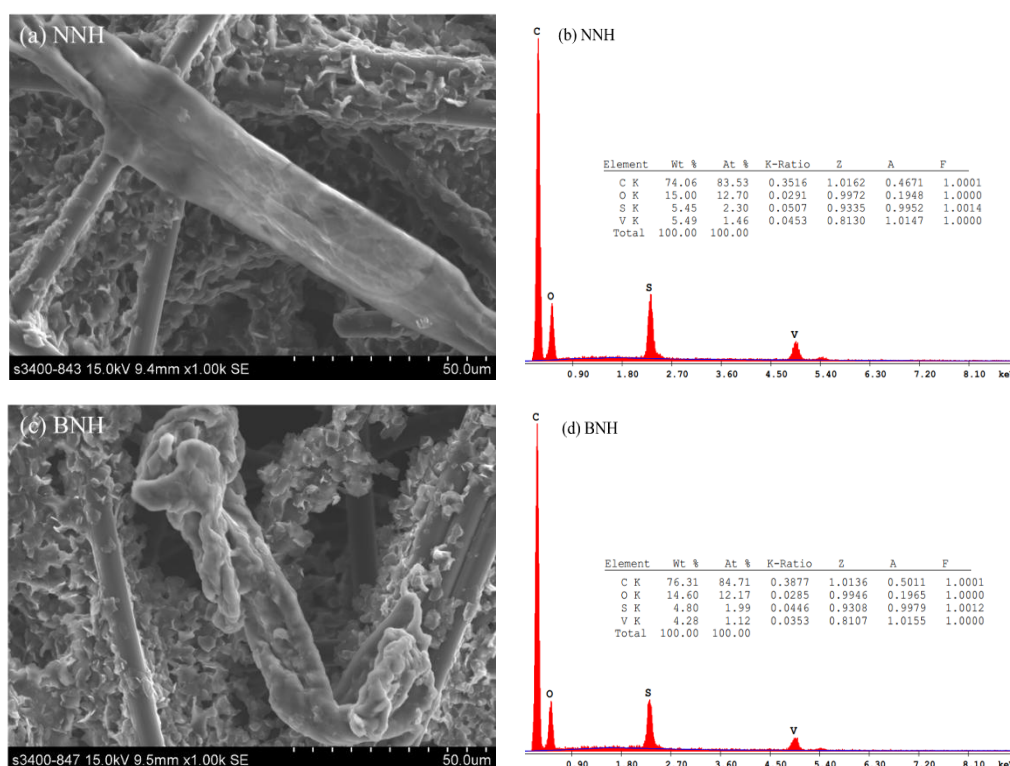


Fig. 5-6 SEM (a, c) and EDX (b, d) of precipitation on the NE under NNH and BNH conditions

To complement the spectroscopic evidence, post-mortem SEM-EDX analysis was performed on electrodes after cycling. Post-mortem SEM images show continuous, thin, film-like coverage on carbon fibers (Fig. 5-6), observed only for the NNH and BNH cells on the NE and were not observed on the PE. EDX was used to capture the film regions and gave semi-quantitative S/V atomic ratios of 1.58 (NNH) and 1.78 (BNH). Because the bulk electrolyte is 1 M vanadium + 3 M H_2SO_4 ($\text{S}/\text{V} = 3$), a simple dried electrolyte residue would be expected to show $\text{S}/\text{V} \approx 3$ under vacuum-drying (60°C , 2 h; V and S are non-volatile under these conditions). The measured $\text{S}/\text{V} < 3$ therefore argues against residual electrolyte and is consistent with a sulfate-coordinated vanadium-oxide hydrate ($\text{VO}_x(\text{SO}_4)_y \cdot n\text{H}_2\text{O}$), i.e., the film-forming branch schematized in Eq. (5-8) and Eq. (5-9). No specific stoichiometry is claimed, and it is noted that $\text{V}_x\text{O}_y \cdot n\text{H}_2\text{O}$ may co-exist, because oxygen in EDX can include contributions from the aged carbon substrate, and thus EDX alone cannot distinguish between these two solid phases.

The combined optical microscopy, Raman, and SEM-EDX data demonstrate the

heterogeneous nature of electrode surface precipitation. According to the precipitation pathways outlined in Eq. (5-2) to Eq. (5-9), VO_2^+ ions can undergo hydrolysis and condensation to form polymeric vanadium oxo species, which may further densify or partially order into domains consistent with vanadium oxo and/or vanadyl-sulfate coordination. Therefore, the precipitation observed in amorphous regions is more appropriately described as gel-like vanadium oxo aggregates with possible nanoscale ordering, rather than a well-defined crystalline phase. Such structural heterogeneity typically develops under moderately acidic conditions where spatial pH fluctuations during electrochemical cycling allow hydrolysis and crystallization to occur simultaneously.

This precipitation has two critical electrochemical consequences. First, the carbon fiber pores are physically blocked, diminishing the real ECSA and leading to an abrupt rise in the charge transfer overpotential. Second, the mass transport pathways are obstructed within the electrode, so that mass transport is limited and the overpotential therefore increases sharply. These factors together rationalize the significantly higher overpotentials observed under NNH and BNH conditions and confirm that the sharp non-linear increase in the total overpotential is associated with real precipitation on the NE rather than a measurement error.

The combined structural and spectroscopic evidence (optical microscopy, Raman, and SEM-EDX) is therefore used primarily qualitatively to support these mechanistic interpretations, namely precipitation-induced pore blocking, loss of real ECSA, and obstruction of mass transport pathways. Although the observed trends are consistent with changes in charge transfer and mass transport behavior, a direct quantitative correlation between, for example, the amount or thickness of the precipitated layer and specific electrochemical parameters has not yet been established. Establishing such quantitative structure performance relationships would require additional systematic experiments and image analysis and is identified as an important topic for future work, while the present chapter focuses on providing a consistent qualitative framework and quantitative overpotential decomposition in Section 5.3.

5.3 Decomposition of overpotentials

The presence of vanadium oxide precipitation, as established by the morphological and spectroscopic evidence in Section 5.2, suggests a strong correlation with the electrochemical behavior of the cells. Specifically, the accumulation of precipitation under NNH and BNH conditions is expected to influence various components of the total cell overpotential, including ohmic resistance, charge transfer kinetics, and mass transport processes. To elucidate these effects, the overall cell overpotential was decomposed into its individual contributions by EIS. As in Chapter 4, the details of this method are given in Section 2.5.3. Since the overpotential decomposition method has been confirmed under BH and PNH conditions without precipitation (Fig. 5-2) and verified on the V^{2+}/V^{3+} side in Chapter 4, the following decomposition can be shown to be reliable.

5.3.1 Charge transfer overpotential

Fig. 5-7 shows the Nyquist plots measured at open-circuit voltage (OCV) for the four heat treatment conditions, with the R_{ohm} subtracted from each spectrum for clarity; thus, the high frequency intercept of each curve is set to zero. The plot shows the negative imaginary impedance ($-Z''$) versus the real impedance (Z') for four conditions: BH (black squares), PNH (red circles), NNH (blue triangles), and BNH (green inverted triangles). The main plot has axes from 0.0 to 0.6 $\Omega \text{ cm}^2$ for Z' and 0.0 to 0.6 $\Omega \text{ cm}^2$ for $-Z''$. An inset plot shows a zoomed-in view of the low-frequency region with axes from 0.000 to 0.150 $\Omega \text{ cm}^2$ for Z' and 0.000 to 0.150 $\Omega \text{ cm}^2$ for $-Z''$. Another inset plot shows a zoomed-in view of the high-frequency region with axes from 0.0 to 0.150 $\Omega \text{ cm}^2$ for Z' and 0.0 to 0.150 $\Omega \text{ cm}^2$ for $-Z''$. The curves show a semi-circular arc in the main plot, with the BNH condition showing the largest arc and the BH condition showing the smallest arc.

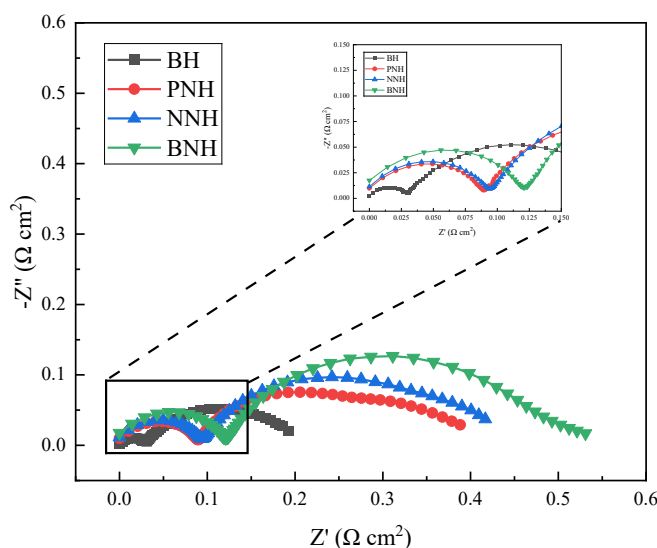


Fig. 5-7 Nyquist plots of OCV conditions

It is evident that the size of the first semicircle (corresponding to the charge transfer process) varies substantially among the four conditions, following the trend: BNH > NNH > PNH > BH. This directly indicates that the R_{ct} was reduced after heat treatment, and the effects of the positive and the negative sides are different. As described in Section 2.5.5, based on the equivalent double layer capacitance C_{eff} , effective ECSA (A_{eff}) and reaction rate constant k_0 could be calculated.

Table 5-1 Effective electrode area and reaction rate constant

Heat treatment condition	Normalized A_{eff}	$k_0 / 10^{-4} \text{ cm s}^{-1}$
BH	216.56 ± 20.38	0.81 ± 0.04
PNH	24.33 ± 1.49	2.98 ± 0.13
NNH	23.43 ± 1.27	2.58 ± 0.14
BNH	11.95 ± 0.93	3.83 ± 0.21

The A_{eff} for the four heat treatment conditions is summarized in Table 5-1. Among them, the BH condition exhibits the highest A_{eff} , while PNH and NNH are similar and intermediate, and BNH is the lowest. The substantial increase in A_{eff} upon heat treatment can be attributed to several factors. First, high temperature treatment effectively removes residual binder, thereby exposing carbon fibers that were previously covered, and enhancing the accessible porosity of the carbon paper (see Section 3.2). This is also reflected in the measured bulk porosity, which increases from 0.857 to 0.886 after heat treatment (see Section 3.4.2). Additionally, thermal processing at 500 °C induces the formation of surface pits and roughened features on the carbon fibers, which further increases the available reaction area.

The normalized A_{eff} for the four electrode configurations (BH, PNH, NNH, and BNH) exhibit an approximate ratio of 18.1: 2.0: 2.0: 1. Notably, the A_{eff} of BH is nearly nine times higher than that of either PNH or NNH. This pronounced difference suggests that, although single-sided heat treatment (i.e., PNH or NNH) can enhance the A_{eff} on the treated side, the overall

effective area remains severely limited by the not-heated electrode. In other words, the benefits of increased A_{eff} cannot be fully realized unless both electrodes are heat treated. Furthermore, the A_{eff} values for PNH and NNH are almost identical, indicating that the enhancement in effective surface area induced by heat treatment is not selective for VO^{2+} or VO_2^+ ions under the present symmetric cell configuration.

The k_0 for the four electrode configurations (BH, PNH, NNH, and BNH) are approximately 1: 3.7: 3.2: 4.7. It is evident that heat treatment in air does not result in a significant improvement in k_0 for the $\text{VO}^{2+}/\text{VO}_2^+$ redox couple but rather restricts the redox reaction. Traditionally, it is recognized that oxygen introduced during air activation can generate surface oxygen functional groups, which are expected to enhance k_0 by increasing the redox-active sites [19]. For the $\text{V}^{2+}/\text{V}^{3+}$ redox couple, such an effect has indeed been observed [20]. However, in the case of the $\text{VO}^{2+}/\text{VO}_2^+$ system, vanadium ions can be adsorbed onto polar oxygenated groups on the carbon surface, locally passivating the electrode and thus hindering the redox conversion [21,22]. This surface interaction likely accounts for the relatively higher k_0 values observed for not-heated electrodes, and the lack of correlation between k_0 and A_{eff} under air-treated conditions.

According to the literature [23], VO_2^+ is easily adsorbed onto oxygenated surfaces but desorbs less readily, which can lead to the accumulation of a passivation film. In contrast, VO^{2+} is less likely to be adsorbed and more easily desorbed, resulting in only a thin passivation film. In the PNH condition, the PE is not heated, and the NE is heat-treated, thus containing more oxygen functional groups. During charging, VO_2^+ is reduced to VO^{2+} at the NE, and since the generated VO^{2+} desorbs quickly, only a thin passivation film is expected to form. In the NNH condition, the PE is heat treated, and the oxidation of VO^{2+} to VO_2^+ occurs there. Here, the generated VO_2^+ remains adsorbed on the oxygenated surface, leading to a thicker passivation film and a more significant suppression of redox kinetics, resulting in a lower k_0 compared to PNH. Overall, these adsorption-desorption behaviors explain the stronger inhibitory effect of heat treatment on VO^{2+} oxidation than on VO_2^+ reduction.

The charge transfer overpotential calculated based on the R_{ct} obtained by EIS separation is shown in Fig. 5-8.

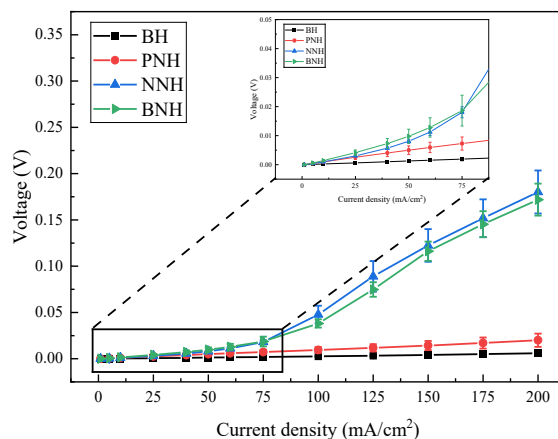


Fig. 5-8 Charge transfer overpotential calculated from EIS

Fig. 5-8 shows the charge transfer overpotentials calculated from the charge transfer resistance (R_{ct}) obtained by EIS. The relative magnitudes of charge transfer overpotentials under all current densities follow the order $BNH > NNH > PNH > BH$, which is determined by a combined effect of ECSA and k_0 , both of which are influenced by electrode heat treatment.

At low current densities ($< 75 \text{ mA/cm}^2$), for the BH condition, it achieves the lowest charge transfer overpotential, despite exhibiting the smallest k_0 . This is attributed to its substantially enlarged ECSA, which more than compensates for the reduction in k_0 , allowing for the minimal activation polarization. In contrast, the BNH condition displays the highest charge transfer overpotential. Although it has the largest k_0 , its ECSA is extremely limited, leading to excessive current localization and high polarization. For the PNH and NNH conditions, both ECSA and k_0 assume intermediate values. However, though the ECSA is similar in both cases, PNH shows a slightly higher k_0 , resulting in lower charge transfer overpotential, especially at low current densities.

At higher current densities (NNH: 100 mA/cm^2 , BNH: 125 mA/cm^2), a significant increase in charge transfer overpotential is observed, which corresponds to the onset of η_{prc} .

associated with the precipitation of vanadium oxo species, possibly involving sulfate coordination. The accumulation of the precipitation leads to partial blockage of electrode pores and a further reduction in the effective ECSA, thereby increasing the charge transfer resistance and accelerating overpotential growth. Notably, this additional overpotential component is not captured by conventional EIS-based separation, reflecting the limitation of EIS in directly detecting side reactions within the cell.

These findings indicate that neither ECSA nor k_0 alone determines activation polarization. On the contrary, it is the combined effect that determines the observed trends. This also explains discrepancies in the literature regarding the effect of heat treatment on $\text{VO}^{2+}/\text{VO}_2^+$ charge transfer overpotential: depending on the carbon electrode type and the specifics of the heat treatment, the relative changes in ECSA and k_0 may not always align, which is different from the consistent increase typically seen for the $\text{V}^{2+}/\text{V}^{3+}$ couple. This is consistent with previous studies. Bourke et al. [2,8] demonstrated on glassy carbon electrodes that oxidative treatments suppress the k_0 of the $\text{VO}^{2+}/\text{VO}_2^+$ couple. Bachman et al. [8] further reported that in rayon-based carbon felts, thermal oxidation increased surface area but introduced oxygen functional groups that suppressed k_0 , resulting in higher positive electrode overpotentials. In the PAN-based, highly graphitized carbon paper, however, the substantial increase in ECSA upon heat treatment outweighed the reduction in k_0 , leading to a net decrease in the charge transfer overpotential for the BH condition. This explains why the difference between BH and PNH, though moderate (46 mV at 200 mA/cm²), remains measurable. Overall, these results highlight that while oxidative modification consistently suppresses k_0 for the $\text{VO}^{2+}/\text{VO}_2^+$ couple, the overall impact on electrode performance depends strongly on the carbon substrate and the balance between kinetic suppression and surface area gain.

5.3.2 Mass transport overpotential

The mass transport overpotential calculated based on the R_{mt} ($R_{\text{mt1}} + R_{\text{mt2}}$) obtained by EIS separation is shown in Fig. 5-9.

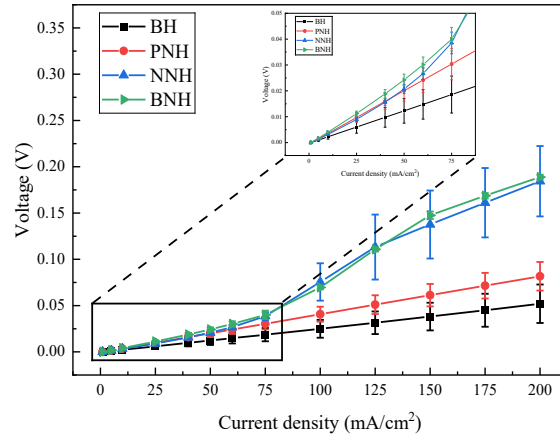


Fig. 5-9 Mass transport overpotential calculated from EIS

Fig. 5-9 shows the mass transport overpotentials for all four conditions. Across the entire current density range, the relative magnitudes follow the order $\text{BNH} > \text{NNH} > \text{PNH} > \text{BH}$, though the difference between NNH and BNH becomes more pronounced at higher current densities. In the low current density region ($< 75 \text{ mA/cm}^2$), the mass transport overpotentials for PNH and NNH are nearly identical and fall between those of BH and BNH.

At low current densities ($< 75 \text{ mA/cm}^2$), the BH condition exhibits the lowest mass transport overpotential, while BNH shows the highest. This can be attributed to the enhanced porosity and significantly improved wettability introduced by heat treatment, which promote more efficient electrolyte transport. For both PNH and NNH, the mass transport overpotentials are very similar, suggesting that single-sided heat treatment has an equivalent effect on the $\text{VO}^{2+}/\text{VO}_2^+$ redox couple. As described in Eq. (2-30) and Section 4.3.2, when δ_{eff} can be considered close to that in the case of single-sided heat treatment, the effective diffusion coefficient D_{eff} of vanadium ions based on the intrinsic diffusivity determines the k_m^{app} and the mass transport overpotential at a given current density. Thus, this similarity can be explained by the fact that the intrinsic diffusion coefficients of VO^{2+} and VO_2^+ ions are close ($4.22 \times 10^{-6} \text{ cm}^2/\text{s}$ and $4.03 \times 10^{-6} \text{ cm}^2/\text{s}$, respectively, according to [24]), so the heat treatment has a comparable influence on the effective diffusion coefficients under these conditions.

At higher current densities (NNH: 100 mA/cm^2 , BNH: 125 mA/cm^2), the mass transport

overpotentials for NNH and BNH rise sharply, consistent with the onset of precipitation caused by the lack of heat treatment at the negative electrode. The resulting pore blockage substantially inhibits electrolyte transport, creating sharper local concentration gradients. Notably, while NNH displays an earlier onset of this effect, at even higher current densities ($\geq 150 \text{ mA/cm}^2$), the mass transport overpotential of BNH exceeds that of NNH. This may be attributed to the absence of heat treatment on the positive electrode in BNH, resulting in a higher mass transport overpotential at the PE side compared to NNH.

5.3.3 Ohmic overpotential

The calculated ohmic overpotentials for all electrode treatment conditions are presented in Fig. 5-10, including contributions from the electrolyte, ion-exchange membrane, electrodes, and cell interfaces.

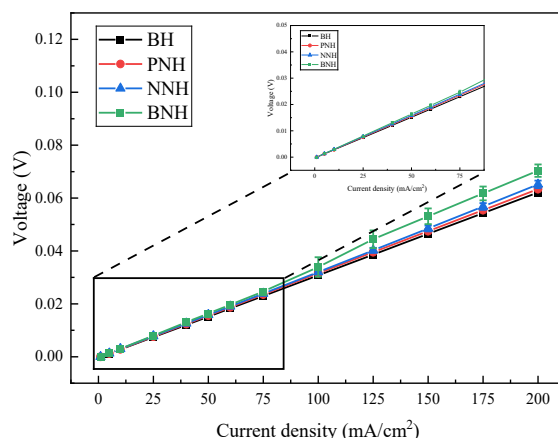


Fig. 5-10 Ohmic overpotential calculated from EIS

Fig. 5-10 shows that the ohmic resistance remains essentially constant across all current densities, averaging $0.33 \pm 0.02 \Omega \text{ cm}^2$ for all electrode configurations. The BH condition exhibits the lowest ohmic resistance, while PNH and NNH conditions yield slightly higher values, and BNH exhibits the highest; however, these differences are minimal.

To further elucidate the origins of ohmic resistance, the membrane's ionic resistance was quantitatively estimated. For the ion conductivity of the Nafion 117 membrane, 1 M vanadium +

5 M H₂SO₄ electrolyte has been reported as 0.051 S/cm and 0 M vanadium + 5 M H₂SO₄ has been reported as 0.075 S/cm [25], while 0 M vanadium + 3 M H₂SO₄ has been reported as 0.108 S/cm [26]. Assuming the effect of vanadium ions on conductivity is proportional at different acid concentrations, the membrane conductivity κ under the experimental condition (1 M vanadium + 3 M H₂SO₄) was estimated as 0.073 S/cm. Assuming that the ionic conductivity of the Nafion 211 (25 μ m thickness) membrane is similar to that of the Nafion 117 membrane, the membrane resistance in the experimental system was calculated to be 0.034 Ω cm², accounting for approximately 10.3% of the total ohmic resistance. This small fraction arises from the comparatively high membrane conductivity at moderate vanadium and acid concentrations.

The majority of the ohmic resistance arises from ionic conduction through the electrolyte and the porous electrode structure. The effective ionic conductivity of 1 M VOSO₄ + 3 M H₂SO₄ has been reported as 432 mS/cm [27]. The calculated ionic resistance, based on the effective ionic conductivity (342.7 mS/cm for not-heated electrodes, calculated using the Bruggeman relation [28]) and a cell gap of 0.08 cm (thickness of the carbon paper and membrane), was 0.233 Ω cm², accounting for approximately 70.6% of the total area-specific ohmic resistance (0.33 Ω cm²). After heat treatment, the electrode porosity increased slightly from 0.857 to 0.886, resulting in a modest increase in effective ionic conductivity to 360.3 mS/cm and a corresponding decrease in ionic resistance to 0.220 Ω ·cm². Nevertheless, the limited extent of binder removal and relatively short treatment duration minimized the practical reduction in total ohmic resistance.

Additionally, incomplete electrolyte wetting within electrode pores can further elevate ohmic resistance, even with high bulk electrolyte conductivity. The remaining contribution (about 21% of the total) is primarily attributed to electrode-current collector interfacial resistance, which is determined by electrode compression, surface roughness, and assembly quality. These factors together limit the impact of electrode heat treatment on the overall ohmic resistance.

5.3.4 Overall cell performance

The reliability of the EIS-derived overpotential separation was first confirmed by (i) the

previous study on the V^{2+}/V^{3+} couple [29] and (ii) the agreement between the summed calculated components η_{EIS} and the experimentally measured η_{tot} under the BH and PNH conditions (see Fig. 5-4), demonstrating that the method is applicable to the present VO^{2+}/VO_2^+ system.

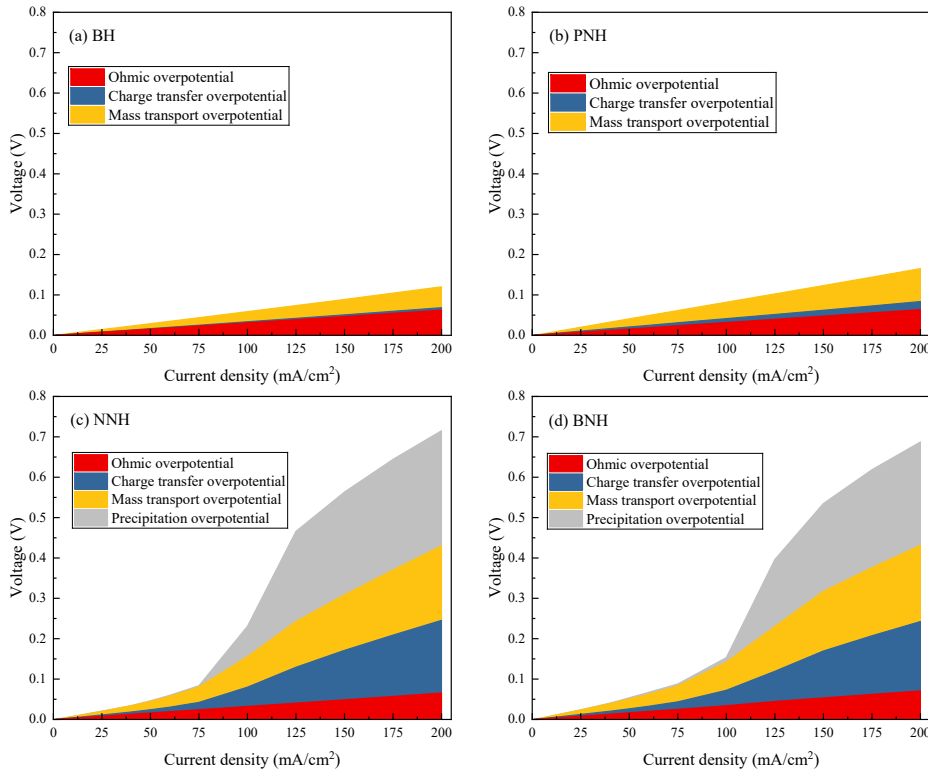


Fig. 5-11 Overpotential decomposition analysis (a) BH (b) PNH (c) NNH (d) BNH

Fig. 5-11 (a, b) displays the overpotential separation for the BH and PNH conditions over 0-200 mA/cm². In both configurations, the charge transfer overpotential is consistently the smallest contribution, which confirms that heat treatment effectively mitigates reaction-kinetic barriers. For the BH condition, the ohmic overpotential shows the largest contribution across all current densities. Both-electrode heat treatment enlarges the ECSA and improves wettability, thereby lowering the charge transfer overpotential and the mass transport overpotential simultaneously. Because heat treatment has small effects on the cell's intrinsic electronic and ionic resistance, the ohmic resistance becomes the dominant loss once the other two overpotentials are reduced. For the PNH condition, the mass transport overpotential becomes the largest term. The

not-heated positive electrode retains its hydrophobic surface, hindering electrolyte penetration and creating pronounced concentration gradients, leading to transport limitations outweighing both the ohmic drop and the already-reduced kinetic barrier.

Fig. 5-11 (c, d) shows that when the negative electrode is left not-heated (NNH and BNH), the precipitation overpotential appears once the current density exceeds the threshold current density (NNH: 100 mA/cm², BNH: 125 mA/cm²). Before the precipitation threshold, the mass transport overpotential is roughly twice the charge transfer overpotential, indicating that concentration gradients dominate the losses. After precipitation occurs, charge transfer overpotential grows faster than mass transport overpotential and the two terms become comparable by 200 mA/cm². This trend shows that the precipitation attributed to vanadium oxo species, possibly involving sulfate coordination, blocks active sites and reduces the ECSA to a greater extent than it impedes transport pathways. The effect is more obvious in the NNH cell, consistent with its higher precipitation rate observed in Fig. 5-4.

Overall, it is evident that heat treatment of carbon electrodes markedly lowers both the charge transfer and the mass transport overpotentials in the VO²⁺/VO₂⁺ system. This process is especially critical for the electrode on which VO₂⁺ is reduced (the negative side in the symmetric cell); omitting this treatment allows precipitation to occur and to quickly limit the performance.

5.4 Conclusions

This study systematically investigated the impact of electrode heat treatment on the electrochemical behaviors and performance stability of the VO²⁺/VO₂⁺ redox reaction using symmetric VRFB cells. These results show a representative case for SGL 39AA carbon paper under 500 °C air treatment. Under precipitation-free conditions, EIS enabled decomposition of the total overpotential into charge transfer, mass transport, and ohmic components. Recognizing that conventional EIS underestimates added losses during non-steady precipitation, an operational precipitation overpotential η_{prc} was introduced to capture the evolving contribution beyond the equivalent circuit terms. Further characterization techniques, including SEM, Raman

spectroscopy, optical microscopy, and XPS, were utilized to elucidate the underlying mechanisms.

(1) Heat treatment increased the effective ECSA but tended to decrease the apparent k_0 for $\text{VO}^{2+}/\text{VO}_2^+$, consistent with stronger adsorption of vanadium species at surface oxygen functional groups introduced by heat treatment. Ultimately, the combined influence of increased ECSA and decreased k_0 determined whether the charge transfer overpotential was increased or decreased under different electrode conditions.

(2) Heat treatment substantially improved electrode wettability, enhancing electrolyte penetration and markedly reducing the mass transport overpotential. Conversely, insufficient heat treatment resulted in pronounced concentration gradients due to limited electrolyte accessibility, highlighting the essential role of hydrophilic surface modification.

(3) Omitting heat treatment at the negative electrode triggered precipitation at relatively low current densities (100-125 mA/cm²), consistent with the rise of η_{prc} , Nyquist abnormal plots, and non-stationary voltage-time traces. Poor wettability limited proton resupply, elevating local pH and facilitating the formation of vanadium-oxo/vanadyl-sulfate hydrates that blocked pores, reduced the available ECSA, and increased both charge transfer and mass transport losses.

Overall, this work clarifies how electrode heat treatment influences charge transfer, mass transport, ohmic and precipitation processes in the $\text{VO}^{2+}/\text{VO}_2^+$ system, helping to explain the previously inconsistent findings in the literature. In particular, it highlights the importance of heat treatment of the electrode where VO_2^+ reduction occurs, as this effectively suppresses precipitation and maintains electrochemical stability. While the trends reported here are grounded in a specific substrate and heat-treated method, the mechanistic insights provide a basis for rational design of high performance and long-lasting VRFB electrodes.

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Chapter 6

Comparison Between the V^{2+}/V^{3+} and VO^{2+}/VO_2^+ Symmetric Cells

6.1 Introduction

This chapter compares the two half reactions of the vanadium redox flow battery under identical experimental conditions. The purpose is to clarify how heat treatment influences the key parameters and overall performance of the electrodes. By summarizing the results from both sides, the discussion identifies which factors are responsible for performance improvement and which remain unchanged or even become worse. The comparison includes the ohmic resistance, charge transfer and mass transport parameters, and the precipitation behavior on the positive side. These factors together determine how the carbon electrodes respond to heat treatment under different operating current densities.

The discussion also examines how asymmetric electrode modification leads to unbalanced reactions. Understanding these relationships helps explain differences in current distribution, overpotential allocation, and the onset of side reactions. The following sections present a step-by-step comparison of characteristic parameters, followed by a contribution analysis of the different overpotentials. Through this analysis, the influence of electrode treatment is connected to the overall performance and stability of the system. Chapter 6 therefore provides an integrated perspective that links material properties, electrochemical behavior, and system-level performance between the two half reactions.

6.2 Charge transfer intrinsic parameters

This section compares kinetic parameters under identical geometry, compression, temperature, and SOC. The effective surface area A_{eff} was obtained from the double-layer method (Eq. (2-15)). The intrinsic rate constant was reported as k_0 and, for cross-system use on the positive electrolyte, as the proton-normalized k_0^* (Eq. (2-17) and Eq. (2-18)). The effective volumetric reaction rate constant (reaction rate per unit electrode volume) $A_{\text{eff}}k_0^*$ was also

calculated to reflect the comprehensive reaction ability of the carbon electrode. Results are shown for the four configurations BH, PNH, NNH, and BNH.

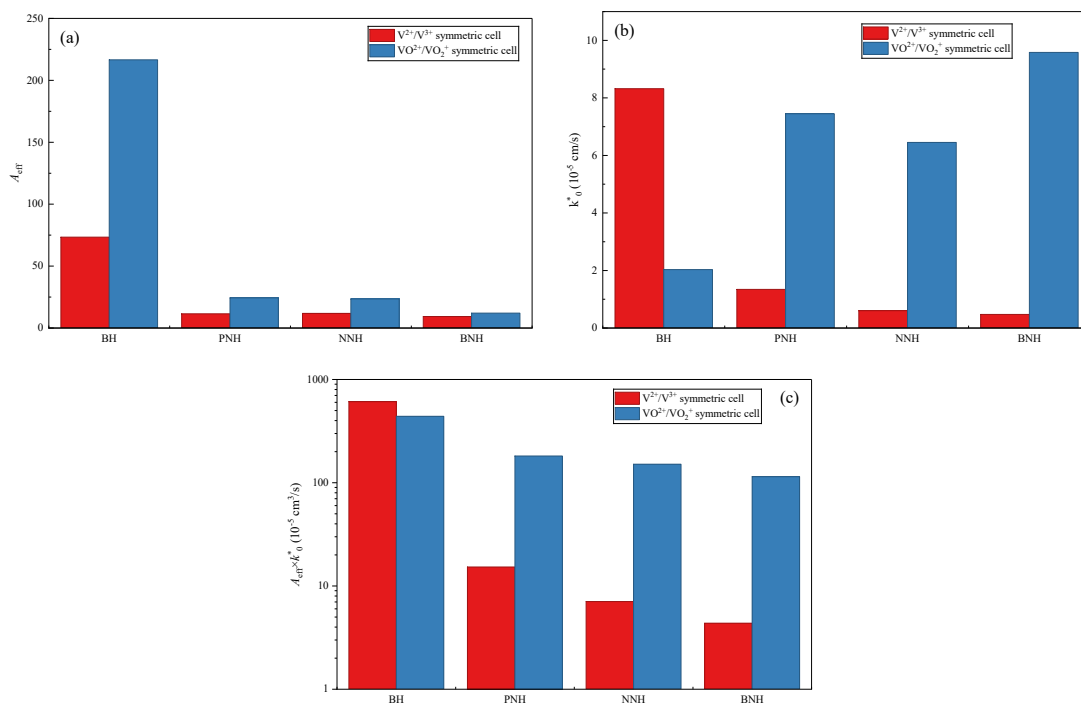


Fig. 6-1 Comparison of charge transfer intrinsic parameters (a) A_{eff} (b) k_0^* (c) $A_{\text{eff}}k_0^*$

Fig. 6-1a shows the effective electrochemical surface area A_{eff} . The VO^{2+}/VO_2^+ symmetric cell shows a larger A_{eff} than the V^{2+}/V^{3+} cell under all configurations, which is consistent with contact angle tests. On the unheated electrode, the contact angle for the negative electrolyte ($V^{2.5+}$) is 113.6° , significantly greater than the contact angle for the positive electrolyte (79.2°) (see Fig. 3-6). Although the carbon electrode is hydrophobic to both $V^{2.5+}$ and $V^{4.5+}$ electrolytes before heat treatment, it is evident that it is more hydrophobic toward the $V^{2.5+}$ electrolyte. The carbon electrode surface with stronger hydrophobicity cannot be fully wetted, resulting in a low A_{eff} . After heat treatment, both show strong hydrophilicity; however, the relative wetting order remains, as reflected by the larger A_{eff} for the positive electrolyte. The difference is most pronounced under the BH condition. A_{eff} increases from the BNH and single-sided cases (PNH and NNH) to the BH condition for both electrolytes, which is consistent with

improved wettability and a larger fraction of accessible pores.

Fig. 6-1b compares the proton-normalized intrinsic rate constant k_0^* . The ordering differs from the A_{eff} result. For the $\text{V}^{2+}/\text{V}^{3+}$ couple, k_0^* is highest under the BH condition and decreases when one side or neither side is heated. For the $\text{VO}^{2+}/\text{VO}_2^+$ couple, k_0^* is highest when neither carbon electrode is heat-treated. Under the BH condition, the positive k_0^* is lower than in the other configurations. This pattern indicates that the negative half reaction benefits strongly from heat treatment activation of intrinsic sites, whereas the positive reaction shows a weaker or even adverse response in intrinsic kinetics when both electrodes are heat-treated, despite the larger accessible area.

It is worth mentioning that under the BH conditions, the k_0^* of $\text{V}^{2+}/\text{V}^{3+}$ is higher than that of $\text{VO}^{2+}/\text{VO}_2^+$, which is contrary to some earlier reports [1–3]. This may be because the reported k_0^* values for vanadium ions on carbon electrodes are highly sensitive to the carbon type and electrode pretreatment, leading to large variations when these conditions are not standardized [4]. If the electrode treatment conditions are not standardized, the k_0^* of $\text{V}^{2+}/\text{V}^{3+}$ and $\text{VO}^{2+}/\text{VO}_2^+$ are often not comparable. In addition, commonly used electrochemical measurement methods such as CV may use the geometric surface area of the electrode instead of A_{eff} to calculate k_0^* , which can lead to a significant overestimation of k_0^* , especially under the conditions for porous electrodes.

Figure 6-1c reports the volumetric kinetic factor $A_{\text{eff}}k_0^*$ with a logarithmic vertical axis. The BH condition gives the largest values for both couples. Under the BH condition, the $\text{V}^{2+}/\text{V}^{3+}$ reaction is slightly higher than the $\text{VO}^{2+}/\text{VO}_2^+$ reaction, indicating that the intrinsic activation on the negative side outweighs the area advantage of the positive side. In single-sided and untread conditions (PNH, NNH, BNH) the $\text{VO}^{2+}/\text{VO}_2^+$ side exceeds the $\text{V}^{2+}/\text{V}^{3+}$ side by about one order of magnitude. The $\text{V}^{2+}/\text{V}^{3+}$ couple shows a very strong dependence on heating the negative electrode: $A_{\text{eff}}k_0^*$ rises by two orders of magnitude from BNH to BH and is larger in PNH than in NNH. The $\text{VO}^{2+}/\text{VO}_2^+$ couple benefits primarily from accessible area: BH remains the highest

because the large A_{eff} compensates for the smaller k_0^* , while any heating (PNH or NNH) already provides a substantial gain over BNH. The negative side is limited mainly by intrinsic kinetics and requires both-heated activation, whereas the positive side is governed by interfacial accessibility.

To consider concentration effects, the apparent exchange current density i_0 was also calculated. According to Eq. (2-16), i_0 was obtained directly from the fitted charge transfer resistance R_{ct} .

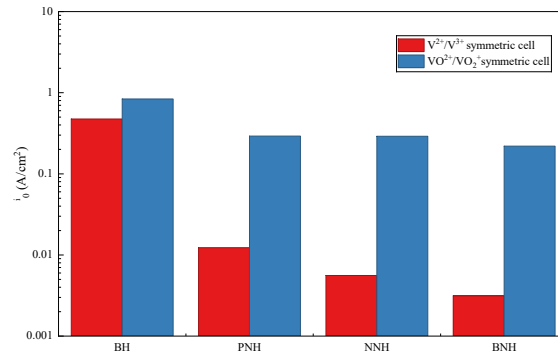


Fig. 6-2 Comparison of i_0

Fig. 6-2 shows that the apparent exchange current density i_0 has a different trend from $A_{\text{eff}}k_0^*$. According to Eq. (2-16), i_0 was obtained directly from the fitted charge transfer resistance R_{ct} and therefore inherently includes the concentration term of the reacting species. It is found that under all four configurations (BH, PNH, NNH, BNH), i_0 of the $\text{VO}^{2+}/\text{VO}_2^+$ symmetric cell is higher than that of V^{2+}/V^{3+} , while $A_{\text{eff}}k_0^*$ shows the opposite only under the BH condition. This difference arises from the actual electrolyte compositions: 1.7 M V + 4.3 M H_2SO_4 for the negative side and 1.0 M V + 3.0 M H_2SO_4 for the positive side. In the V^{2+}/V^{3+} reaction, sulfuric acid acts only as the supporting electrolyte, whereas in the $\text{VO}^{2+}/\text{VO}_2^+$ reaction it participates in proton-coupled electron transfer, so the effective activity term in i_0 becomes larger for the positive couple. Consequently, i_0 is consistently higher for $\text{VO}^{2+}/\text{VO}_2^+$ under every configuration, reflecting the distinction between intrinsic reactivity represented by $A_{\text{eff}}k_0^*$ and the practical

charge transfer capability under real electrolyte conditions.

Overall, the kinetic comparison reveals distinct control factors for the two half reactions. The V^{2+}/V^{3+} side is limited mainly by intrinsic kinetics, while the VO^{2+}/VO_2^+ side is limited by the accessible area. Heat treatment improves both sides, but its effect appears through different routes: activation of reaction sites for the V^{2+}/V^{3+} couple and enhancement of reaction area for the VO^{2+}/VO_2^+ couple. When both electrodes are heated, the two factors act simultaneously, leading to the highest overall reaction rate. The intrinsic index $A_{\text{eff}}k_0^*$ represents the electrode's inherent reactivity, while the apparent exchange current density i_0 reflects the practical charge transfer capability including concentration effects. The combination of these two parameters provides complementary insights into system-level kinetics, linking the intrinsic and operational perspectives.

6.3 Mass transport limitation

This section compares the mass transport capacity of the two half reactions under identical geometry and flow conditions. Rather than relying on theoretical diffusion limitation, the apparent limiting current i_{lim} and the corresponding k_m^{app} were derived consistently from the mass transport overpotential. These indicators reflect the net effect of diffusion and convection together with electrolyte-electrode interactions, without explicit corrections for individual properties such as diffusivity or viscosity, thereby emphasizing relative transport ability across electrolytes and electrode treatments. The results are used to assess how heat treatment and electrolyte type shift the overall transport capability of the porous electrodes.

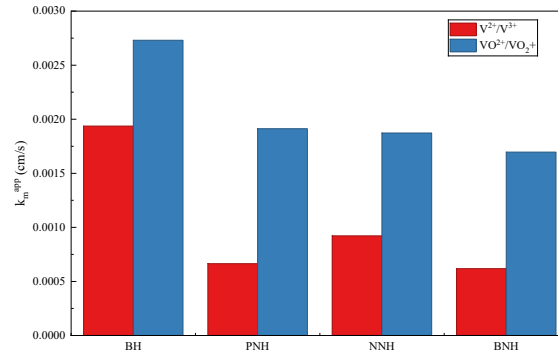


Fig. 6-3 Comparison of mass transport behavior at 50 mA/cm²

To avoid the precipitation effects on the VO^{2+}/VO_2^+ side (which occur at 100mA/cm²), Fig. 6-3 shows the apparent mass transport coefficient k_m^{app} at 50 mA/cm². It is observed that the VO^{2+}/VO_2^+ side is consistently higher than that of the V^{2+}/V^{3+} side across all electrode conditions. The difference is most pronounced under single-sided or unheated conditions (PNH, NNH, and BNH), where the ratio of k_m^{app} (VO^{2+}/VO_2^+ to V^{2+}/V^{3+}) is to 2.9, 2.0, and 2.8, respectively, while under BH conditions, the two remain closer, with a ratio of 1.4. These results indicate that the V^{2+}/V^{3+} system is more sensitive to incomplete heat treatment, exhibiting a sharper reduction in k_m^{app} when wettability and pore accessibility are limited. In contrast, the VO^{2+}/VO_2^+ system maintains relatively high transport capability even without full heat treatment, suggesting that its mass transport performance is less sensitive to effective diffusivity and wetting under the present operating conditions.

Overall, the observed trend of $BH > NNH \approx PNH > BNH$ confirms that heat treatment improves mass transport performance for both redox couples, though the effect is more pronounced on the negative side. Moreover, below the precipitation threshold of the positive electrolyte, the apparent k_m^{app} reflects the usable transport capacity determined by the combined effects of diffusion, convection, and pore utilization. These results highlight that enhanced surface wetting and effective pore activation are the key factors governing the mass transport performance of porous electrodes in VRFBs.

6.4 Ohmic resistance

Based on the discussion of ohmic resistance in Sections 4.3.3 and 5.3.3, the total ohmic resistance was decomposed into electrolyte resistance R_{ele} , membrane resistance R_{mem} , and contact resistance R_{con} . R_{ele} and R_{mem} were obtained by Eq. (2-21), while R_{con} was obtained by subtracting them from the total ohmic resistance. R_{ele} and R_{mem} were normalized, while R_{con} was left unchanged. It is worth noting that since the ohmic resistance of the four symmetrical cell configurations changes very little before and after heat treatment ($0.44 \pm 0.025 \Omega \text{ cm}^2$ for the $\text{V}^{2+}/\text{V}^{3+}$ symmetric cell, and $0.33 \pm 0.02 \Omega \text{ cm}^2$ for the $\text{VO}^{2+}/\text{VO}_2^+$ symmetric cell), this section does not discuss the effects of different heat treatment conditions on ohmic resistance but focuses on the different effects of positive and negative electrolytes.

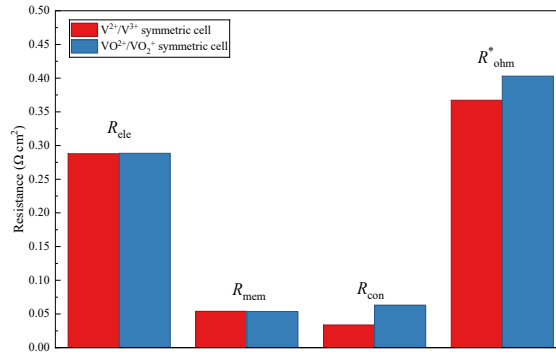


Fig. 6-4 Corrected ohmic resistance decomposition

Fig. 6-4 shows that the electrolyte and membrane components are nearly identical for the two symmetric cells after normalization, which demonstrates the accuracy of the normalization of ionic conductivity based on electrolyte concentration. The remaining difference comes from contact resistance R_{con} . R_{con} is $0.0335 \Omega \text{ cm}^2$ for the $\text{V}^{2+}/\text{V}^{3+}$ symmetric cell and $0.063 \Omega \text{ cm}^2$ for the $\text{VO}^{2+}/\text{VO}_2^+$ symmetric cell. R_{ohm}^* of the positive side is therefore higher after correction, which is different from the total ohmic resistance R_{ohm} before correction, highlighting the influence of the difference in ionic conductivity caused by electrolyte concentration on the ohmic resistance.

This result indicates that the higher ohmic loss on the positive side originates from interfacial contact rather than bulk conduction through the electrolyte or the membrane. The difference is consistent with the more oxidative environment of the positive electrolyte and with known sensitivity of contact resistance to surface chemistry, for example, carbon electrodes can form a passivation film for vanadium ions after oxidation [5]. These factors can increase real contact resistance even when the bulk pathways remain unchanged.

In summary, the ohmic contribution shows minimal variation in the electrolyte and membrane parts across the two couples. The measurable difference lies mainly in the contact term, which dominates the difference in ohmic loss between the two redox couples.

6.5 Unified dimensionless overpotential comparison

To enable a direct and system-level comparison between the V^{2+}/V^{3+} and VO^{2+}/VO_2^+ symmetric cells, the total overpotential is decomposed into ohmic (η_{ohm}), charge transfer (η_{ct}), mass transport (η_{mt}), and precipitation (η_{prc} , when applicable) components under identical geometric and thermal conditions. The relative fractions $f_i = \eta_i/\eta_{tot}$ were evaluated at two representative current densities: 50 mA/cm² (within the pre-precipitation region) and 200 mA/cm² (beyond the precipitation onset for the positive electrolyte). This representation enables visualization of how the relative balance of losses evolves from a stable operating range to a precipitation-influenced condition. At 50 mA/cm², the comparison reflects the intrinsic balance between charge transfer, mass transport, and ohmic contributions, while at 200 mA/cm², the emergence of the precipitation component reveals the degradation of transport uniformity and interfacial stability. These fractional comparisons provide a unified and physically interpretable framework to assess how heat treatment and electrolyte type cooperatively determine the overall energy distribution and limitation behavior of the two vanadium redox systems.

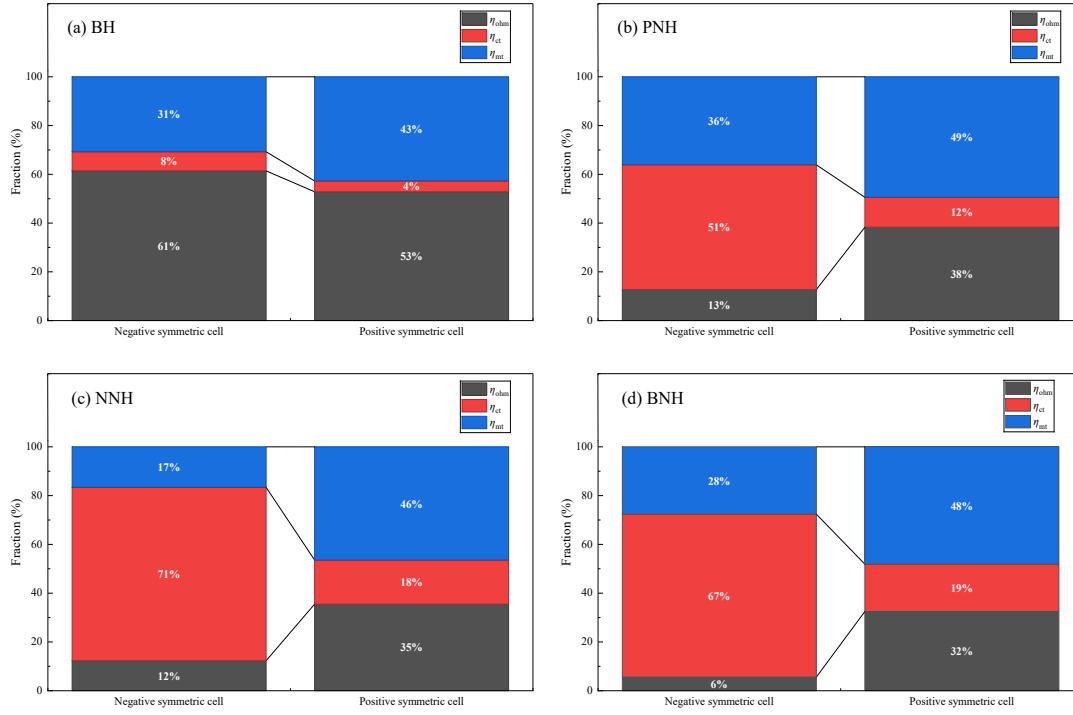


Fig. 6-5 Fractional contributions of overpotential components at 50 mA/cm² for symmetric cells under different electrode treatments.

Fig. 6-5 shows that the relative contributions of η_{ohm} , η_{ct} , and η_{mt} between the V^{2+}/V^{3+} and VO^{2+}/VO_2^+ symmetric cells at the fixed current density of 50 mA/cm², where no precipitation occurs in the VO^{2+}/VO_2^+ electrolyte. Under the BH condition, both systems exhibit a dominant ohmic contribution (≈ 50 -60%) and relatively small activation losses ($< 10\%$), indicating efficient charge transfer. As heat treatment becomes incomplete (PNH, NNH, BNH), the fraction of η_{ct} markedly increases in the negative electrolyte, reaching 50-70%, while that of η_{mt} also rises modestly, suggesting that insufficient surface activation and limited wettability significantly impede interfacial kinetics and mass transport. In contrast, the VO^{2+}/VO_2^+ system maintains lower η_{ct} and higher η_{mt} fractions across all configurations, reflecting intrinsically faster interfacial kinetics but stronger diffusion constraints in the electrolyte. From Sections 4.3.3 and 5.3.3, the ohmic resistance was shown to vary only slightly among different conditions. Therefore, the fractional contribution of the η_{ohm} is mainly governed by the magnitudes of the charge transfer

and mass transport losses. When both η_{ct} and η_{mt} are small, the relative share of η_{ohm} naturally becomes more dominant.

Overall, the evolution from BH to PNH/NNH to BNH demonstrates that heat treatment primarily suppresses kinetic polarization on the negative side, whereas the positive side is governed by transport-related losses even at low current density. These results highlight that the balance between interfacial activation and porous-electrode transport determines the overall electrochemical efficiency of both vanadium redox couples.

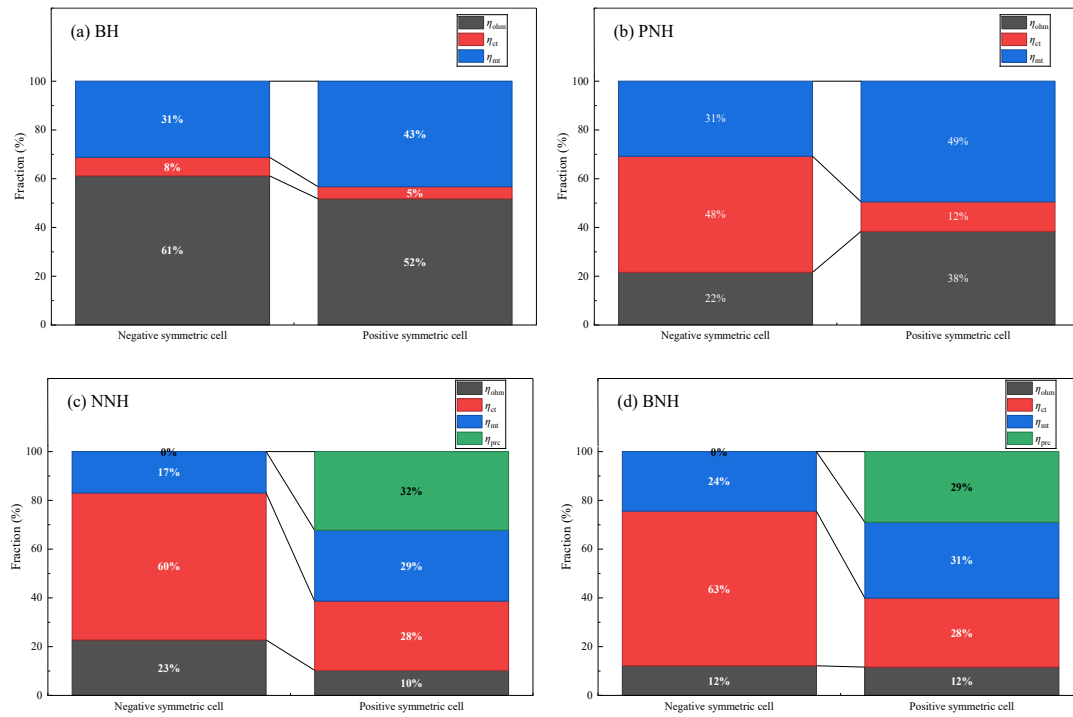


Fig. 6-6 Fractional contributions of overpotential components at 200 mA/cm² for symmetric cells under different electrode treatments.

Fig. 6-6 shows that at 200 mA/cm², the fractional contributions η_{ohm} , η_{ct} , η_{mt} , and η_{prc} losses diverge markedly between the two symmetric cells. Under the BH conditions, both sides remain primarily ohmic-dominated (≈ 50 -60 %) with minor activation losses (< 10 %), indicating stable contacts and efficient charge transfer. As heat treatment becomes incomplete (PNH, NNH, BNH), the negative electrolyte shows a pronounced shift toward kinetic control, with η_{ct} rising

to about 48-63 % and η_{mt} increasing moderately, consistent with limited surface activation and pore wetting. On the positive side, transport and precipitation become dominant under NNH and BNH, where η_{prc} contributes about 30% and η_{ohm} falls to about 10%.

Compared with the 50 mA/cm² condition, while the negative side's polarization mainly increases through kinetic limitation, the positive side experiences an extra rise of 0.25 V associated with the onset of precipitation, which becomes a distinct and irreversible contributor to the total loss. Meanwhile, under NNH and BNH conditions, precipitation significantly affects activation process, resulting in a 10% increase in the charge transfer contribution ratio compared to 50 mA/ cm². By contrast, the effect on mass transport is not significant, resulting in a decrease in the mass transport ratio by approximately 15%. As confirmed in Sections 4.3.3 and 5.3.3, the ohmic resistance itself changes little across configurations; thus, the decreasing ohmic fraction (20-25%) primarily reflects the rapid growth of kinetic, transport, and precipitation losses at high current densities.

Overall, the transition from 50 to 200 mA/cm² indicates that the dominant limiting mechanism of the V^{2+}/V^{3+} reaction remains kinetically controlled across all electrode conditions. On the VO^{2+}/VO_2^+ side, the mechanism under the BH and PNH conditions is largely unchanged, but under NNH and BNH, it shifts from mass transport limitation to precipitation-driven kinetics, emphasizing the distinct impact of precipitation formation on the overall overpotential. In summary, when the heat treatment is asymmetric, both half reactions exhibit increased instability under high current operation, highlighting the importance of balanced electrode activation for maintaining system durability.

6.6 Summary

This chapter compares the two half reactions under identical geometry, compression, temperature, and SOC. The aim is to relate heat treatment to changes in charge transfer, mass transport, ohmic, and precipitation (when applicable) behavior and to establish a fair, system-level comparison between the V^{2+}/V^{3+} and VO^{2+}/VO_2^+ symmetric cells. Thus, two complementary

levels are used: (1) parameter-level indicators: conductivity-normalized ohmic resistance, ECSA-based rate constants (and the corresponding apparent exchange current density i_0), and the apparent mass transport coefficient k_m^{app} derived from η_{mt} ; (2) overpotential-level contributions: stacked fractions f_j are evaluated at fixed current densities (50 and 200 mA/cm²).

The analyses show distinct limitations on each side. The $\text{V}^{2+}/\text{V}^{3+}$ couple is mainly kinetically controlled across conditions. Also, heat treatment increases i_0 by activating surface sites, thereby reducing η_{ct} . The $\text{VO}^{2+}/\text{VO}_2^+$ couple is controlled by interfacial accessibility and mass transport, with heat treatment improving wetting/contact and thus lowering η_{mt} . Consistent with Sections 4.3.3 and 5.3.3, the ohmic resistance varies only slightly, and the $\text{VO}^{2+}/\text{VO}_2^+$ side is slightly larger due to the larger contact resistance.

The contribution fraction shows that at 50 mA/cm² (pre-precipitation), the $\text{VO}^{2+}/\text{VO}_2^+$ side shows a larger k_m^{app} and higher mass transport fraction, whereas the $\text{V}^{2+}/\text{V}^{3+}$ side exhibits a larger kinetic fraction. At 200 mA/cm², divergence becomes pronounced: the $\text{V}^{2+}/\text{V}^{3+}$ side remains kinetically limited, while on the $\text{VO}^{2+}/\text{VO}_2^+$ side precipitation appears under NNH and BNH, introducing a distinct η_{prc} component and amplifying the total polarization compared with 50 mA/cm². Under BH and PNH, the positive side remains transport-dominated without a precipitation contribution.

In summary, the two symmetric cells exhibit complementary effects: $\text{V}^{2+}/\text{V}^{3+}$ is governed by activation, whereas $\text{VO}^{2+}/\text{VO}_2^+$ is governed by interfacial accessibility and precipitation when the negative side is not heated. Practically, heat treatment should prioritize raising i_0 on the $\text{V}^{2+}/\text{V}^{3+}$ side and improving wetting while avoiding precipitation on the $\text{VO}^{2+}/\text{VO}_2^+$ side. The combined framework of fractional overpotentials at fixed currents provides a unified, physically grounded basis for cross-system comparison of different chemistries and electrode treatments.

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Chapter 7

Conclusions & Perspectives

7.1 Conclusions

This thesis compares the negative and positive half reactions of the VRFB under identical geometry, compression, temperature, and SOC. The main aim is to clarify how heat treatment modifies the key electrochemical processes, including charge transfer, mass transport, ohmic losses, and precipitation (when accessible), and to establish a unified framework that enables fair cross-system comparison. Thus, symmetric cells are employed to isolate each half reaction, and the intrinsic parameters, exchange current, mass transport coefficient, and overpotentials decomposed by EIS, are systematically analyzed on the same operational basis. To enable quantitative comparison, this study constructs a normalized framework, where charge transfer, mass transport, and ohmic contributions are referenced to common physical quantities: ionic conductivity, ECSA-based rate constant, and an apparent mass transport coefficient. This approach preserves the physical meaning of each term while enabling a consistent comparison across electrode treatments and between the two redox couples. The main findings of each chapter are summarized below.

Chapter 1 states the problem and motivation. The need is for a fair and transparent comparison between two half reactions that often use different electrolytes and surface chemistry. Prior studies have reported mixed conclusions because experimental methods and electrode areas were not aligned. This chapter fixes the scope and defines the main questions about how heat treatment changes surface and transport properties and how to compare the two sides on the same basis. It also reviews different carbon electrode treatment methods reported in the literature, summarizes their typical effects on surface chemistry, structure and electrochemical performance, and then justifies the symmetric cell approach focusing on different overpotentials.

Chapter 2 establishes the experimental protocol and the common normalization scheme.

Symmetric cells are used to isolate each half reaction while keeping geometry, compression, flow, membrane, and 50% SOC fixed. Four configurations (BH, PNH, NNH, BNH) separate the effects of heat treatment. Electrodes are characterized by SEM-EDX, Raman, XPS, contact angle, and gravimetric porosity to quantify wettability, functional groups, and accessible ECSA with repeated measurements to ensure reproducibility. Polarization steps and EIS at OCV and under load are fitted with minimal, stable equivalent circuits. From the fitted area-specific resistances, the charge transfer, mass transport, and ohmic contributions are obtained by numerical integration of $R_x(i)$. A unified normalization removes electrolyte concentration effects: ohmic loss is referenced to ionic conductivities, kinetics are compared by ECSA-based k_0 (with proton-normalized k_0^* when needed), and mass transport is assessed using the mass transport coefficient. Moreover, all overpotential contributions are scaled to identify the dominant one. Therefore, these evaluation methods provide a comprehensive approach to the roles of charge transfer, mass transport, ohmic losses, and precipitation, thereby providing a fair platform for comparison in subsequent chapters.

Chapter 3 shows how air heat treatment at 500 °C changes the carbon paper at the material level. The electrode shifts from a binder-rich, hydrophobic surface to a more open, rough, and hydrophilic one. SEM indicates binder decomposition and fiber surface roughening that open blocked pores and expose new surface. Raman and XPS show higher disorder and a several-fold increase in oxygen functional groups, adding edge and defect sites and increasing surface polarity. Contact angle tests confirm a strong gain in wettability; electrolytes penetrate rapidly after treatment. Porosity rises modestly, improving ionic pathways without degrading electronic conduction through the fiber network. These changes increase accessible ECSA, provide more reactive sites, and ease electrolyte access, which together explain the lower charge transfer resistance, faster kinetics, and better tolerance to high current that are analyzed for each half reaction in Chapters 4 and 5.

Chapter 4 analyzes the V^{2+}/V^{3+} half reaction with symmetric cells and separate charge

transfer, mass transport, and ohmic contributions. A simple EIS-based procedure is used and agrees well with I-V analysis. The results show that the intrinsic kinetics are not the same for the two ions: V^{3+} reduction is slower than V^{2+} oxidation under the same conditions, so they are treated separately in analysis. The diffusion coefficients also differ; in the concentrated electrolyte used here V^{3+} diffuses faster than V^{2+} , which appears as higher mass transport overpotential when V^{2+} is the reacting species. Heat treatment improves performance by activating reaction sites and enhancing wettability and porosity. The kinetic gain is stronger for V^{3+} reduction, while the transport gain is stronger for V^{2+} . Single-sided heat treatment creates electrode mismatch and limits improvement, so uniform treatment is preferred. These findings provide a clear benchmark for the negative side and set up the comparison with the positive side in Chapter 5.

Chapter 5 examines the VO^{2+}/VO_2^+ half reaction with symmetric cells and focuses on how heat treatment changes traditional three overpotentials and stability. Under conditions without precipitation, EIS separates the three overpotentials. To capture non-steady losses during precipitation, an operational precipitation overpotential η_{prc} is defined. Heat treatment increases effective ECSA but tends to lower the apparent k_0 because vanadium species absorb more strongly on oxygen functional groups formed during heat treatment and the net charge transfer depends on this balance. Wettability improves markedly, electrolyte penetration increases, and mass transport loss falls; however, when treatment is insufficient, concentration gradients grow. Omitting heat treatment at the electrode where VO_2^+ is reduced leads to early precipitation around 100-125 mA/cm², with poor wetting limiting proton resupply, pore blockage by vanadium-oxo/vanadyl-sulfate hydrates and rises in both charge transfer and mass transport losses. Overall, the chapter explains why the literature reports different performance trends when carbon electrodes undergo heat treatment and shows that heat treatment of reduction-side electrode is key to suppressing precipitation and maintaining stable performance for the VO^{2+}/VO_2^+ system.

Chapter 6 provides a comprehensive comparison on a common basis using parameter-level indicators (conductivity-corrected ohmic resistance, ECSA-based rate constants and

apparent exchange current i_0 , and the apparent mass transport coefficient k_m^{app} derived from η_{mt}) together with overpotential decomposition at fixed current densities. The kinetic analysis shows consistently larger activation losses on the negative side in all configurations, matching the ordering of i_0 . Mass transport is evaluated from k_m^{app} in the pre-precipitation region and by stacked overpotential fractions at 50 and 200 mA/cm², showing significant enhancement of negative side after heat treatment. The ohmic analysis, after conductivity correction, shows that the electrolyte and membrane contributions are similar and that the remaining differences arise from interfacial contact resistance. Over the stable operating range (50 mA/cm²), the two systems display comparable transport fractions, whereas at 200 mA/cm² the positive side develops an additional precipitation-related component that increases total polarization. These common results reveal distinct differences: activation limits the negative side; accessible area and contact dominate the positive side, and precipitation further contributes at high current densities.

In summary, this study builds a continuous link from material modification to system performance. Heat treatment changes the structure, chemistry, and wettability of carbon electrodes, which in turn modify charge transfer, mass transport, and ohmic behaviors, and thereby affect the corresponding overpotentials. When the total overpotential is decomposed into its individual components through EIS analysis, these contributions can be evaluated on a unified and quantitative basis, allowing the two half reactions, $\text{V}^{2+}/\text{V}^{3+}$ and $\text{VO}^{2+}/\text{VO}_2^+$, to be directly compared within the same framework. On this basis, the original contributions of this thesis can be summarized in four points:

(1) Symmetric-cell platform with four heat treatment configurations for half-reaction analysis:

A symmetric-cell platform with four electrode treatment configurations (BH, PNH, NNH, BNH) was established and validated for both the $\text{V}^{2+}/\text{V}^{3+}$ and $\text{VO}^{2+}/\text{VO}_2^+$ couples under identical geometry and operating conditions. This provides a stable alternative to conventional three-electrode setups and enables half-reaction-level comparison of positive and negative electrodes

and different electrode modification strategies.

(2) Integrated framework to decompose overpotentials and identify precipitation-related polarization:

By combining galvanostatic polarization with EIS analysis, the total cell overpotential was separated into charge transfer, mass transport, and ohmic components under practical current densities, and an additional precipitation-related contribution was defined and linked to experimentally observed vanadium-oxide deposits. This framework offers an operational diagnostic for precipitation-dominated conditions, especially on the positive side.

(3) Quantification of intrinsic half-reaction asymmetry and ion-selective response to thermal activation:

Under unified conditions, the kinetic and transport behaviors of all four vanadium ions were quantified, showing that the two half-reactions within the same redox couple are not equivalent. The same heat treatment protocol was found to benefit the negative couple (increased active surface area and apparent reaction rate) but to reduce the apparent reaction rate of the positive couple despite increased surface area, revealing an ion-selective “compensation” profile of thermal activation.

(4) Heat treatment and electrode-pairing guidelines based on bottleneck-side identification:

Using normalized indicators that combine conductivity, active surface area, and overpotential decomposition, the kinetic or transport bottleneck side was identified for each electrode pairing. The analysis explains why single-sided heat treatment can destabilize operation and trigger early precipitation, and it leads to practical heat treatment and electrode-pairing guidelines that can be applied to high power VRFB operation.

7.2 Perspectives

This work clarifies how heat treatment affects each half reaction, establishes a unified comparison framework for the two vanadium couples, and proposes practical heat treatment and

electrode-pairing guidelines. While the present study focuses on steady-state conditions with fixed concentrations and symmetric cells, several directions remain open for investigation.

First, although time dependence is not the main focus, VRFB electrodes inevitably evolve during operation. Gradual changes in apparent limiting current due to precipitation and slow variations in exchange current during cycling require more detailed tracking. Extending the present framework to time-resolved measurements would enable charge transfer, ohmic, and mass transport parameters (including i_0 and k_m^{app}) to be followed under different currents, directly linking transient changes to shifts in electrochemical performance.

Second, the scope can naturally expand to other chemistries and configurations. The same approach applies to redox couples such as Fe/Cr or Zn/Br, as well as to systems with different membranes or flow fields. Using common evaluation methods and overpotential analysis allows fair comparison even when electrolyte composition, concentration, or viscosity are different. Such tests will clarify which limitations are general and which depend on specific chemistries, providing a consistent way to screen materials and treatments that enhance cell performance.

Third, coupling this framework with modeling can provide further depth. Multiphysics simulations could incorporate the measured i_0 , k_m , and contact parameters to predict how losses distribute in practical cells. Data-driven or AI-assisted methods could then track the onset of precipitation and visualize how the safe operating window shifts during degradation. The combined insight would generate operating maps that indicate where charge transfer, mass transport, and ohmic processes dominate, and how surface treatments modify those boundaries.

Fourth, the same framework also supports practical design. It can guide the selection of heat treatment parameters that increase k_0 on the negative side and improve wettability and effective ECSA on the positive side. It can help define current limitations that avoid conditions leading to precipitation. These guidelines are simple in statement yet practical in application and can be extended from single cells to full stacks and other redox systems.

Finally, the concept established in this work remains consistent and reproducible. It

emphasizes isolating the variables that require correction or normalization, directly comparing those that differ essentially, and examining how material modification shifts the overall electrochemical behavior on a common basis. In this way, laboratory-scale treatments are coherently linked to system-level performance, providing both a foundation for future studies and a framework for rational electrode design.

List of publications

Journal papers related to this thesis (peer-reviewed)

1. **P. Sun**, T. Suzuki, S. Tsushima, Investigation of Kinetic and Mass Transport Behaviors of V^{2+} and V^{3+} Ions Using Symmetric Vanadium Redox Flow Battery Configuration, J Electrochem Soc, 172 (2025) 050520.
2. **P. Sun**, T. Suzuki, S. Tsushima, Investigation of Kinetic and Mass Transport Behaviors of VO^{2+} and VO_2^+ Ions by Using Symmetric Vanadium Redox Flow Battery Configuration, J Electrochem Soc, 172 (2025) 090543.

Oral presentation conferences related to this thesis (first presenter)

1. **P. Sun**, T. Suzuki, S. Tsushima, Understanding the activation and concentration overpotential of negative and positive electrodes in vanadium redox flow batteries by using symmetric cell architecture, PRiME 2024 (246th ECS Meeting) , October 6-11, 2024, Honolulu, U.S.

Other oral presentation conferences (first presenter)

1. **P. Sun**, K. Matsuo, T. Suzuki, S. Tsushima, Charge and discharge characteristics of the vanadium redox flow battery with different anode and cathode flow rates, 60th Japan Heat Transfer Symposium, May 25-27, 2023, Fukuoka, Japan.
2. **P. Sun**, K. Matsuo, M. Alizadeh, P. Charoen-Amornkitt, T. Suzuki, and S. Tsushima, Investigation of polarization in vanadium redox flow batteries with a fluctuating supply of electrolyte solution, 244th ECS Meeting, October 8-12, 2023, Gothenburg, Sweden.
3. **P. Sun**, M. Alizadeh, T. Suzuki, and S. Tsushima, Experimental analysis of overpotential in vanadium redox flow batteries induced by pulsating flow, The International Workshop on Sustainable Energy Conversion Systems (IWSEC), May 29-30, 2024, Kobe, Japan.

4. **P. Sun**, M. Alizadeh, P. Charoen-Amornkitt, T. Suzuki, and S. Tsushima, Experimental analysis of the effect of pulsating flow on the overpotential of vanadium redox flow battery, Third Asian Conference on Thermal Sciences (ACTS 2024), June 23-27, 2024, Shanghai, China.

Other oral presentation conferences

1. P. Aiemsathit, **P. Sun**, M. Alizadeh, Y. Laoonual, P. Charoen-Amornkitt, T. Suzuki, and S. Tsushima, Improving all-vanadium redox flow batteries in flow-through cells through topology optimization of porous electrodes, Third Asian Conference on Thermal Sciences (ACTS 2024), June 23-27, 2024, Shanghai, China.
2. M. Alizadeh, M. Long, **P. Sun**, P. Charoen-Amornkitt, T. Suzuki, and S. Tsushima, Temperature effects on topologically optimized structure of porous reaction-diffusion system, The 33rd International Symposium on Transport Phenomena, September 24- 27, 2023, Kumamoto, Japan.
3. M. Long, M. Alizadeh, **P. Sun**, P. Charoen-amornkitt, T. Suzuki, S. Tsushima, Impacts of pulsating flow on topologically optimized porous reactors in convection-diffusion-reaction systems, 2024 Small Powertrains and Energy Systems Technology Conference. November 4-7, 2024, Bangkok, Thailand.
4. P. Aiemsathit, **P. Sun**, M. Alizadeh, Y. Laoonual, P. Charoen-amornkitt, T. Suzuki, S. Tsushima, Optimal porous electrode structures in all-vanadium redox flow batteries. 2024 Small Powertrains and Energy Systems Technology Conference. November 4-7, 2024, Bangkok, Thailand.

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