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Author(s)	Kamai, Ryo; Nakanishi, Shuji; Hashimoto, Kazuhito et al.
Citation	Journal of Electroanalytical Chemistry. 2017, 800, p. 54-59
Version Type	AM
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Selective electrochemical reduction of nitrogen oxides by covalent triazine frameworks modified with single Pt atoms

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Abstract

The present work demonstrates that a single platinum atom-modified covalent triazine framework hybridized with carbon nanoparticle (Pt-CTF/CP) exhibited selective activity for the electrochemical reduction of nitrogen oxides. Pt-CTF/CP had low nitrate reduction activity, but efficiently catalyzed the reduction of nitric oxide (NO) molecules derived from the decomposition of nitrite. In contrast, a bulk Pt surface exhibited high activity for both reactions. The selectivity of Pt-CTF/CP for NO is likely due to the unique adsorption behavior of hydrogen atoms and/or nitrate ions on the single Pt atoms.

1. Introduction

Platinum (Pt) is a superior catalyst for numerous useful reactions, such as electrocatalytic reactions in fuel cells [1-3] and those involved in exhaust gas purification [4-6]. Pt single-atom catalysts (Pt-SACs) have attracted considerable recent attention for their potential to maximize the efficiency of Pt atom utilization, and because these materials exhibit unique adsorption characteristics for small molecules, resulting in high activity and selectivity [7-13]. For example, Qiao *et al.* [7] reported that Pt-SACs supported on FeO_x have lower CO adsorption energy and higher CO oxidation activity than those of Pt nanoparticles. More recently, we synthesized a Pt-atom-modified covalent triazine framework hybridized with conductive carbon nanoparticles (Pt-CTF/CP), which was inactive for methanol oxidation and selectivity electrocatalyzed hydrogen oxidation even in the presence of dissolved oxygen [14,15]. The unique catalytic properties of Pt-CTF/CP were attributed to the single Pt atoms, which have significantly different adsorption properties from those of bulk Pt metal. However, the knowledge of the electrocatalytic properties of Pt-SACs remains limited.

The electrochemical reduction reactions of nitrogen oxides, such as nitrate (NO_3^-) and nitrite(NO_2^-), are one of the representative reactions to explore the electrocatalytic properties of Pt-SACs for the following reasons: (i) the mechanisms of these reactions have been widely studied on single and polycrystalline Pt electrodes and (ii) the catalytic properties of these materials,

including activity and product selectivity, are reported to depend strongly on the adsorption behavior of reactants, as explained below. Electrochemical nitrogen oxides reduction reactions in acidic solutions proceed through a stepwise mechanism and generate nitrogen gases (N_2) or ammonium ions (NH_4^+), as shown in Scheme 1. In the present work, we put our focus on nitrate reduction to nitrite [Eq(1)] and nitrite reduction reactions [Eqs(2-4)].

We here summarize the mechanism of nitrate and nitrite reduction reactions on bulk Pt surface. For nitrate reduction reactions (NRR), the first step to form nitrite is the *rate-determining step* [Eq(1)] [16,17].

$$NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O \qquad \text{Eq(1)}$$

Groot *et al.* [18] observed an inverse correlation between NRR current and nitrate concentration at high concentrations (> 0.1 M). Based on this result, adsorbed nitrate was speculated to block the surface adsorption of hydrogen and/or water. Therefore, the second adsorbate (hydrogen and/or water) was considered to be essential for the NRR. Taguchi *et al.* [19] also showed that the simultaneous presence of adsorbed hydrogen and nitrate enhances the rate of NRR on Pt electrodes. Based on the previous results, nitrate is likely reduced on the Pt surface by the reaction of adsorbed nitrate and adsorbed hydrogen through a Langmuir-Hinshelwood-type mechanism. Furthermore, as adsorbed nitrate on Pt surface reacted with adsorbed hydrogen, the adsorption behavior of nitrate is clearly important for NRR. The three possible configurations of adsorbed nitrate on bulk Pt surfaces

are monodentate, bidentate, and tridentate, in which nitrate is bound to the surface through one, two, and three oxygen atoms, respectively. From the results of surface-enhanced infrared absorption spectroscopy analysis, Nakata *et al.* [20] suggested that nitrate preferentially adopts a bidentate structure. Yang *et al.* [21] also demonstrated by DFT calculations that the adsorption of nitrate in a bidentate configuration is the most stable (i.e., highest adsorption energy) among these three configurations.

Nitrite, which is formed by the two-electron reduction of nitrate [Eq(1)], is more reactive than nitrate. The nitric oxide (NO) formed by the decomposition of nitrite [Eq(2)] is an electrochemically active species for nitrite reduction reactions in acidic solutions [22]. Pt metal electrodes are known to catalyze NO dimerization and subsequent N_2O formation in the potential range of 0.25–0.6 V through the Eley–Rideal-type mechanism, whereby a solvated NO reacts with a surface-bound NO [23-25] [Eq(3)], whereas NH_2OH gradually became dominant species formed at lower potentials (< 0.25 V) [Eq(4)] [23].

$$2HNO_2(aq) \rightarrow NO(aq) + NO_2 + H_2O \qquad \text{Eq(2)}$$

$$NO(ad) + NO(aq) + 2H^+ + 2e^- \rightarrow N_2O + H_2O \qquad \text{Eq(3)}$$

$$HNO_2(aq) + 5H^+ + 4e^- \rightarrow NH_3OH^+ + H_2O \qquad \text{Eq(4)}$$

Clayborne *et al.* [24] suggested based on the results of DFT calculations that the reaction of solvated NO with surface-bound NO is energetically favorable for the formation of adsorbed (NO)2-dimers,

which then extract a proton from water. Further, in contrast to NRR, the NO adsorbed on atop sites (monodentate) is reported to be the most reactive species for [Eq (3)] [26-28].

As mentioned above, the electrochemical reduction of the nitrogen oxides can be model reactions in electrocatalysts, since the electrocatalytic properties for these reactions are faithfully reflected in the adsorption characteristics of nitrogen species and hydrogen atoms. Here we investigated the electrocatalytic properties of single Pt atoms of Pt-CTF/CP for the reduction of nitrate and nitrite in acidic solutions. The findings presented here demonstrate that nitrite reduction was efficiently catalyzed by Pt-CTF/CP, whereas the NRR was inhibited.

2. Materials and methods

2.1 Catalyst synthesis

A hybrid material consisting of Pt-CTF and conductive carbon nanoparticles (Pt-CTF/CP) was prepared in the same manner as described in our previous report [14]. Briefly, 1.36 g $ZnCl_2$ (Wako), 129 mg 2,6-dicyanopyridine (Sigma-Aldrich) and 129 mg carbon particles (Ketjen Black EC600JD, Lion Corp.) were mixed and then heat treated in a vacuum-sealed glass tube at 400 °C for 21 h. The resulting powder was washed sequentially with 0.1 M HCl, water, tetrahydrofolate and acetonitrile, and then modified with Pt atoms by stirring in 160 mM $K_2[PtCl_4]$ (Wako) at 60 °C for 4 h. The Pt concentration was estimated to be 12 wt% by X-ray photoelectron spectroscopy (XPS).

We also synthesized Pt nanoparticle-deposited CTF (PtNP-CTF/CP) by heating Pt-CTF/CP at 450 °C for 2 h in a hydrogen atmosphere in a quartz tube. The properties of Pt-CTF/CP PtNP-CTF/CP were compared with commercially available 20 wt% Pt/C (HiSPEC3000, Johnson Matthey).

2.2 Electrochemical measurements

All electrochemical measurements were conducted in 0.1 M $HClO_4$ at room temperature using rotating disk electrodes (RDE). Working electrodes were prepared by dispersing each catalyst in 120 μL ethanol and 47.5 μL Nafion solution (5 wt% solution; Aldrich), and the resulting catalyst inks were dropped onto a glassy carbon electrode. The catalyst loading amounts were standardized by the weight of the carbon support (0.40 $mg_{\text{-carbon}}$ cm^{-2}). A Pt wire and Ag/AgCl (sat. KCl) were used as the counter and reference electrodes, respectively. All potentials were converted into the reversible hydrogen electrode (RHE) scale.

3. Results and discussion

3.1 Electrochemical characterizations of Pt-CTF/CP

Using extended X-ray absorption fine structure (EXAFS) spectra and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), we previously

demonstrated that most Pt atoms in Pt-CTF/CP are individually isolated [14]. In contrast, a number of Pt particles (1-5 nm) in PtNP-CTF/CP (Fig. S1a, c) and Pt/C (Fig. S1b, d) were observed by the STEM images. Although cyclic voltammograms (CVs) of Pt-CTF/CP with a lower loading amount of Pt (2.8 wt%) were presented in our previous work [15], here, we examined and compared the current density (j) versus potential (U) characteristics of CTF/CP, Pt-CTF/CP, PtNP-CTF/CP and Pt/C in 0.1 M Ar-saturated $HClO_4$ without any additives (Fig. 1). In the obtained j vs. U curves, a pair of peaks assignable to the adsorption/desorption of under-potentially-deposited hydrogen (upd-H) on Pt atoms in Pt-CTF/CP was not observed (Fig. 1, red curve), whereas upd-H peaks were clearly observed in the range of 0.05 ~ 0.4 V for PtNP-CTF/CP and Pt/C. As the formation of upd-H proceeds on Pt ensemble sites, such as step, three-fold hollow and defect sites [29,30], the absence of adsorption/desorption peaks for upd-H is attributable to the isolation of Pt atoms in Pt-CTF/CP.

Based on the prediction that all Pt atoms in Pt-CTF/CP were isolated and electrochemically active, the total number of Pt atoms on 12 wt% Pt-CTF/CP was estimated to be 1.8×10^{17} cm^{-2}. In contrast, the number of electrochemically active Pt atoms on Pt/C and PtNP-CTF/CP, as calculated from the electric charge for the adsorption of upd-H in CV, was estimated to be 4.5×10^{16} and 3.6×10^{16} cm^{-2}, respectively. Although some of Pt atoms on Pt-CTF/CP may not be exposed to the electrolyte and are therefore electrochemically inactive, the number of active Pt atoms on Pt-CTF/CP would be at least comparable to that on Pt/C and PtNP-CTF/CP.

3.2 Nitrogen oxides reduction by Pt-CTF/CP

3.2.1 Nitrate (NO_3^-) reduction activity of Pt-CTF/CP

The nitrate reduction activity of Pt-CTF/CP was compared to those of PtNP-CTF/CP and 20 wt% Pt/C by measuring *j* vs. *U* curves in 0.1 M $HClO_4$ aqueous solution supplemented with various concentrations of nitrate (Fig. 2). For Pt/C and PtNP-CTF/CP, an increase in the cathodic wave was clearly observed at potentials below 0.4 V, which was a similar potential range as that for the adsorption/desorption of upd-H. These properties were consistent with those previously reported for polycrystalline Pt electrodes [16-18]. In contrast, Pt-CTF/CP generated almost no current at all examined potential regions even in the presence of 1 M nitrate. As Pt-CTF/CP, Pt/C and PtNP-CTF/CP have a similar number of electrochemically active Pt atoms, these results indicate that Pt single atoms had very low electrocatalytic NRR activity.

3.2.2 Nitrite (NO_2^-) reduction activity of Pt-CTF/CP

We next evaluated the nitrite reduction activity of single Pt atoms of Pt-CTF/CP. Fig. 3 shows cyclic voltammograms (Figs. 3a-e) and Faradaic current density vs. *U* curves (Fig. 3f) for the catalytic materials in 0.1 M $HClO_4$ aqueous solution supplemented with nitrite. Although small reduction currents were observed on CP and CTF/CP at potentials of ≤ 0.6 V, the cathodic current

density was clearly enhanced for Pt-CTF/CP, PtNP-CTF/CP and Pt/C. In addition, the current densities of Pt-CTF/CP were approximately two thirds of those of Pt/C at all examined concentrations of nitrite. Taken together, these results indicate that not only bulk Pt surfaces, but also single Pt atoms of Pt-CTF/CP, facilitated the reduction of nitrite. In the Faradaic current density vs. *U* curve for Pt-CTF/CP (Fig. 3f), a change in the slope was observed at 0.25 V, a result that is consistent with the Faradaic current density vs. *U* curves of PtNP-CTF/CP and Pt/C. This increase in Faradaic current is likely because the reaction pathway changed from N_2O formation [Eq(3)] to NH_2OH production [Eq(4)] at 0.25 V, even for Pt-CTF/CP. Based on these results and previously reported findings [23], single Pt atoms of Pt-CTF/CP facilitated the reduction of NO molecules derived from the decomposition of nitrite in a similar manner to bulk Pt. Specifically, the first step of NRR to form nitrite [Eq(1)] was selectively inhibited on single Pt atoms, whereas the subsequent reduction of nitrite was catalyzed by Pt-CTF/CP.

3.3 Nitrate (NO_3^-) adsorption on single Pt atoms of Pt-CTF/CP

Nitrate adsorption on electrodes is required for the reduction of nitrate to nitrite [Eq(1)] [18,19,31]. Thus, to clarify the reason why Pt-CTF/CP exhibited poor NRR activity, we next examined if nitrate ions adsorb on single Pt atoms of Pt-CTF/CP by measuring the oxygen reduction reaction (ORR) activity of this material in the presence of nitrate. The polarization curves for ORR

in the presence of $NaNO_3$ at various concentrations are shown in Fig. . The ORR onset potential was approximately 0.86 V, which was consistent with the finding of our previous study [14]. Although the onset value (0.86 V) was not dependent on the nitrate concentration, a decrease in the diffusion limiting current was observed at higher nitrate concentration (> 0.1 M). Considering that the ORR limiting current in 1 M $NaClO_4$ was clearly larger than that in 1 M $NaNO_3$ (Fig. S2), this property is presumably because the adsorption of O_2 on single Pt atoms in Pt-CTF/CP was inhibited by the adsorbed NO_3^-. Consistent with this speculation, Groot *et al.* [18] reported that the reaction order of NRR on Pt metal became negative at high concentrations (> 0.1 M) because the excess amount of adsorbed nitrate inhibited the adsorption of the second species (hydrogen and/or water) necessary for the reaction to proceed. Thus, although nitrate is able to adsorb on Pt sites of Pt-CTF/CP, the catalyst had no detectable NRR activity.

3.4 Proposed mechanisms of the inactiveness of Pt-CTF/CP for NRR

The reaction mechanism of Pt-CTF/CP is proposed here to gain insight into the selective electrocatalytic properties of Pt-SACs.

As mentioned in the introduction, nitrate is reduced on the Pt surface by the reaction of adsorbed nitrate and adsorbed hydrogen through a Langmuir-Hinshelwood-type mechanism. In addition, considering that the NRR mediated by Pt/C and PtNP-CTF/CP occurred between 0.4 and

0.05 V, which corresponds to the upd-H potential region (Fig. 1 and Fig. 2), the upd-H was considered to be essential for the NRR on bulk Pt surface. However, reversible peaks corresponding to the formation and desorption of upd-H were absent on Pt-CTF/CP (Fig. 1), indicating that single Pt sites are not occupied with adsorbed hydrogen atoms above 0.05 V. Thus, we speculate that Pt-CTF/CP exhibits negligible NRR activity due to a lack of adsorbed protons, which are required for Langmuir-Hinshelwood-type processes. In contrast, only solvated protons are involved in the reductive dimerization of NO (formed by nitrite decomposition) to N_2O [Eq(3)] [22,23]. Thus, adsorbed hydrogen atoms may not be required for the nitrite (NO) reduction reaction on the Pt surface, at least in the potential region where N_2O is formed (> 0.25 V).

Another possible explanation for the inefficiency of Pt-CTF/CP for the NRR is that the nitrate adsorption strength on single Pt atoms is too weak to activate nitrate ions. Based on the Sabatier principle, an optimal electrocatalyst should have moderate binding strength with adsorbate. If the adsorbates bind too strongly, the catalytic active sites are poisoned by the intermediates. In contrast, when they bind too weakly to the catalyst surface, the reaction does not occur because the reactant cannot be activated. The adsorption of nitrate in a bidentate configuration on bulk Pt surfaces (i.e., Pt-O-(NO)-O-Pt) is stronger and more stable than that for nitrate in mono- or tridentate configurations [20,21]. However, the monodentate form of nitrate is considered to be the only permissible configuration on single Pt atoms because of the absence of adjacent Pt sites. Thus, the

nitrate adsorption strength on Pt-CTF/CP is likely weaker than that on bulk Pt surfaces. However, Yang *et al.* [21] showed that the biding strength of nitrate on Pt, even in a bidentate manner, is weaker than that on the optimal catalyst for the reduction of nitrate to nitrite [Eq(1)]. Namely, nitrate is insufficiently activated to be reduced for nitrite on single Pt atoms due to this weak interaction. In contrast, the NO adsorbed on atop sites (monodentate) is reported to be the most reactive species for NO (nitrite) reduction [26-28], and thus it is reasonable to speculate that the NO formed by nitrite decomposition was reduced, even on single Pt sites of Pt-CTF/CP. Further studies aimed at determining the nitrogen oxides reduction mechanism of Pt-CTF/CP by DFT calculations and the NO stripping voltammetry [25] are currently in progress in our laboratory.

4. Conclusions

The present work has demonstrated that although Pt-CTF/CP exhibits almost no detectable NRR activity, the nitrite reduction activity of this hybrid catalytic material is comparable to that of bulk Pt surfaces. Although nitrate reacts with adsorbed hydrogen through a Langmuir-Hinshelwood-type mechanism during the NRR on Pt, the single Pt atoms of Pt-CTF/CP are free from adsorbed hydrogen atoms at upd-H regions due to the lack of Pt ensemble sites, which are needed to stabilize hydrogen atoms. Further, because the nitrate on single Pt atoms of Pt-CTF/CP appears to adopt the monodentate form, which is less stable configuration than bidentate one, nitrate

may have insufficient adsorption energy for its activation. We anticipate that the present novel findings for the nitrogen oxides reduction activities of single Pt sites can be applied towards the sophisticated design of electrocatalysts with high activity and unique selectivity for nitrogen oxides reduction reactions. In addition, our findings suggest that single-metal-atom-modified CTF electrocatalysts can potentially modulate the adsorption properties of adsorbates and be utilized for selective reactions, such as hydrocarbon oxidation reactions.

Acknowledgement

This research was supported by the PRESTO Program of the Japan Science and Technology Agency (JST). We thank Prof. Dr. H. Ishikita (The University of Tokyo, Japan) for fruitful discussions.

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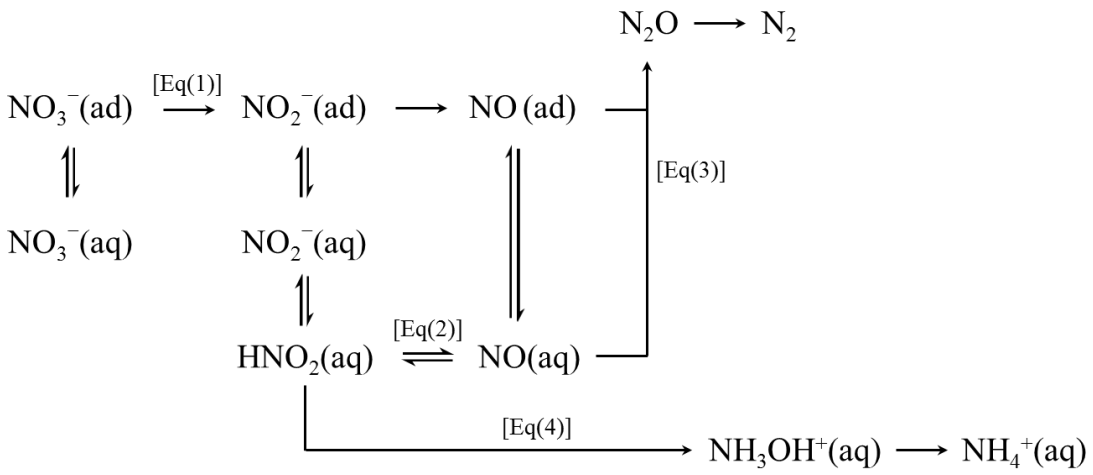
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Scheme 1. Major reaction pathway of electrochemical reduction of nitrogen oxides on Pt electrode.

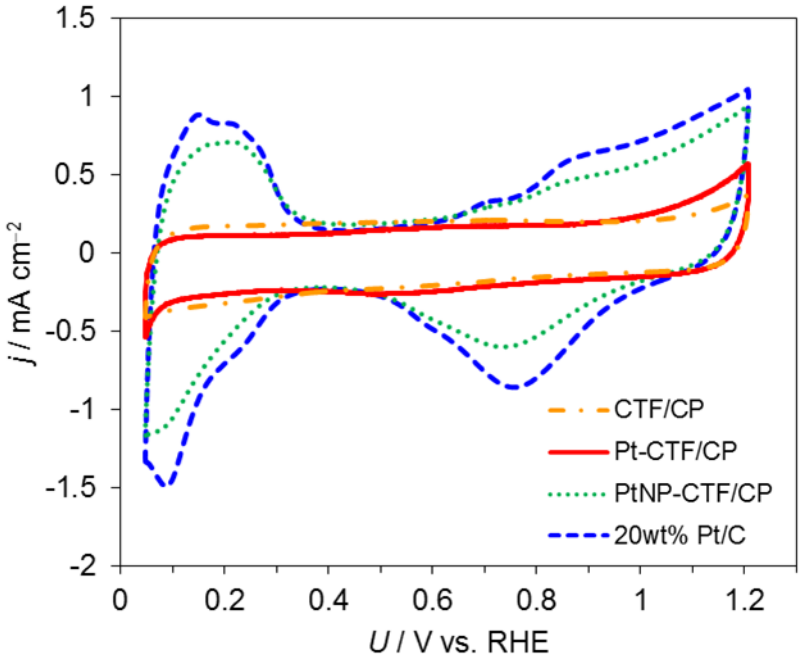


Fig. 2. Cyclic voltammograms of electrodes modified with CTF/CP, Pt-CTF/CP, PtNP-CTF/CP and Pt/C in Ar-saturated 0.1 M $HClO_4$. Scan rate: 10 mV s^{-1}.

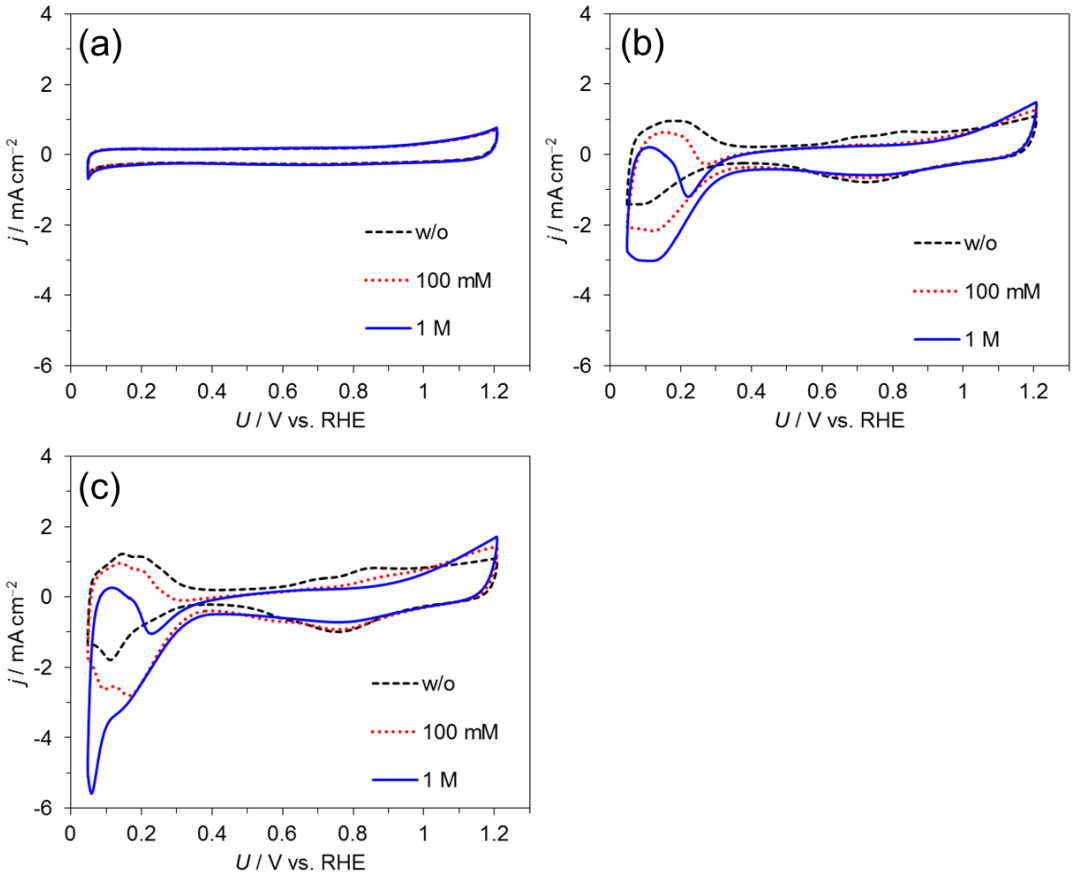


Fig. 3. Cyclic voltammograms of electrodes modified with (a) Pt-CTF/CP, (b) PtNP-CTF/CP and (c) Pt/C in Ar-saturated 0.1 M $HClO_4$ containing the indicated concentrations of $NaNO_3$. Rotation rate: 1,500 rpm. Scan rate: 10 mV s^{-1}.

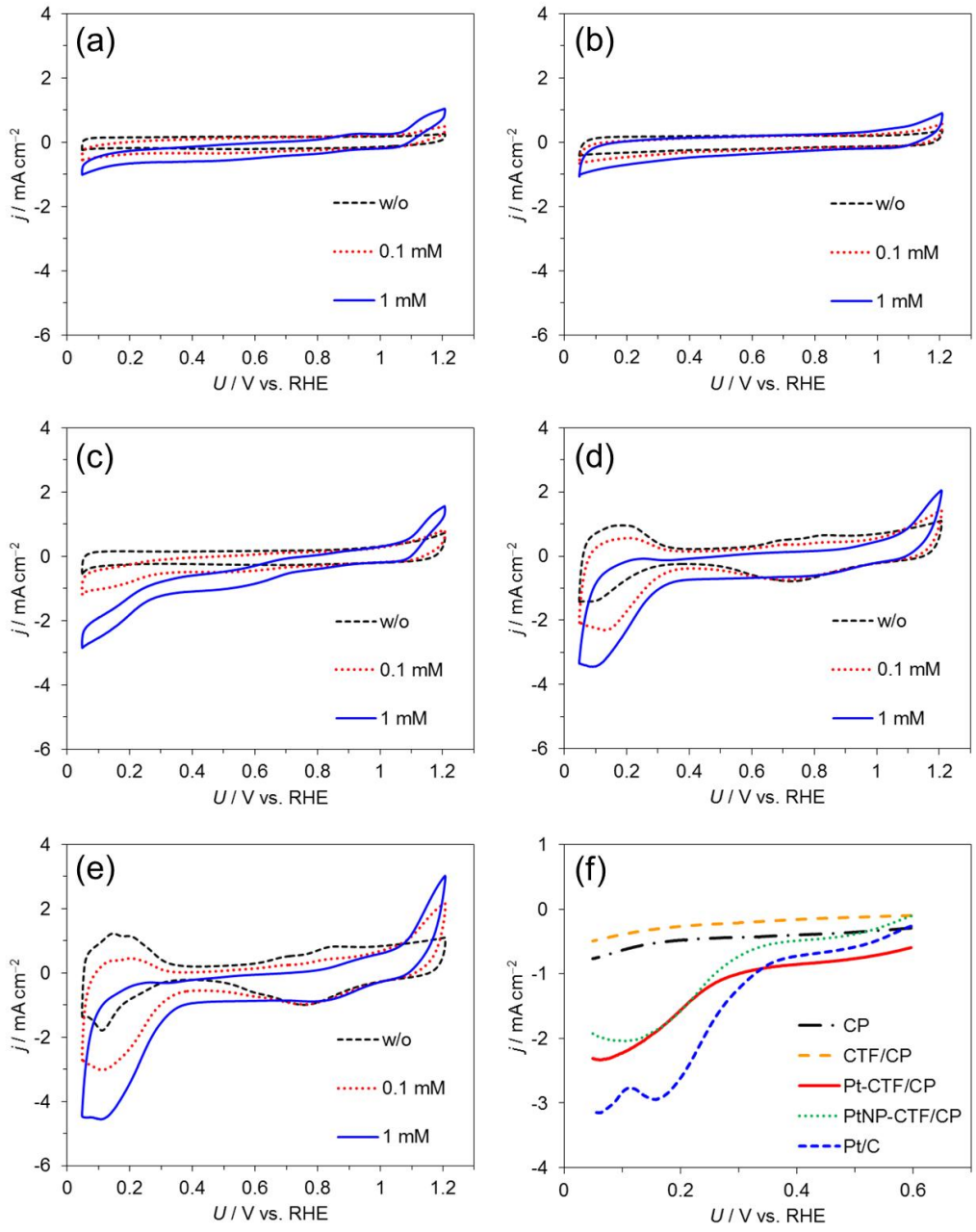


Fig. 4. Cyclic voltammograms of electrodes modified with (a) CP, (b) CTF/CP, (c) Pt-CTF/CP, (d) PtNP-CTF/CP and (e) Pt/C in Ar-saturated 0.1 M $HClO_4$ containing the indicated concentrations of $NaNO_2$, and (f) Faradaic current density vs. potential curves for nitrite reduction reaction in 1 mM $NaNO_2$ scanned from +0.6 V to +0.05 V. Rotation rate: 1,500 rpm. Scan rate: 10 mV s^{-1}. Faradaic currents were calculated by subtracting the current observed when the CVs were performed in electrolyte solutions in the absence of nitrite from the current observed when the CV was performed in electrolyte solutions containing nitrite.

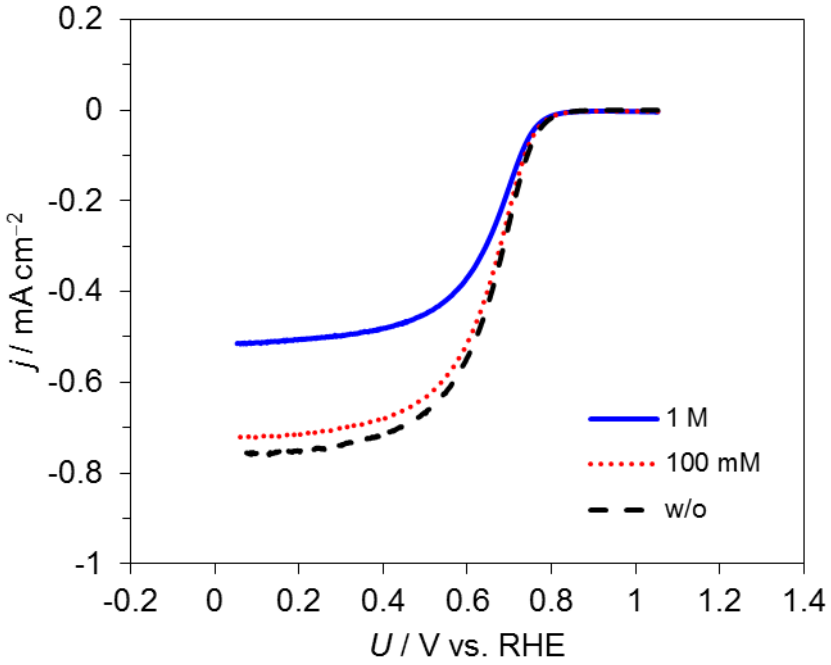


Fig. 5. Polarization curves of Pt-CTF/CP for oxygen reduction reaction in 0.1 M $HClO_4$ containing increasing concentrations of $NaNO_3$. The electrolyte was saturated with mixed gas consisting of 0.2 atm O_2 / 0.8 atm Ar. Rotation rate: 1,500 rpm. Scan rate: 10 mV s^{-1}.