Title	Rechageable Lithium Batteries Using Conductive Polymers
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Citation	電気材料技術雑誌. 2011, 20(2), p. 69-70
Version Type	VoR
URL	https://hdl.handle.net/11094/76880
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電気材料技術雑誌　第20巻第２号
J. Soc. Elect. Mat. Eng.　Vol.20,　No.2　２０１１

Rechageable Lithium Batteries Using Conductive Polymers

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Since 1991, the lithium-ion batteries (LIB) have made progress in its commercialization, remarkably with respect to the number of produced units as well as to battery performance. $LiFePO_4$ has been focused in the world as cathode material for a large scale LIB for electric vehicles. However, electronic conductivity of the pristine $LiFePO_4$ is very low with about 10^{-9} Scm^{-1}. Therefore, for the fabrication of cathode electrode using $LiFePO_4$, the soluble polyaniline (PANI) can be used as binding materials in place of polyvinylidene fluoride (PVdF). Conductive polymer technology has been expected to support the technical innovation for new type batteries.

1. Introduction

Since the principle of secondary batteries by doping of polyacetylene(1) is invented, a polymer battery using polyaniline(2) and polyacene(3) as active material was commercialized. Research and development of these polymer battery , has contributed greatly to the commercialization of "lithium ion battery".

In the last 20 years, the lithium-ion batteries have shown a remarkable and continuous development with respect to the number of produced units as well as to the efficiency and life time. The lithium batteries using polymer electrolyte are also called "polymer batteries". Lithium-ion-type polymer battery composed of $LiMn_2O_4$ positive electrode, 1M $LiPF_6$/EC/DMC gel electrolyte, and carbon negative electrode was developed by Bellcore's gel process(4). This technology is attracting attention as a significant impact on commercialization of polymer battery using a polymer electrolyte.

Recently, the conducting polymers as composite materials of electrode attract much attention, because these polymers are expected to be useful to improve the performance of active material ($LiFePO_4$) of battery electrode, again.

2. Polymer Electrodes

Polypyrole and polyaniline are the most popular and stable conducting polymers, and they are known to have an excellent cycle life as a battery active material. Electrochemical polymerized conducting polymer have a high rate charge-discharge characteristic as a positive electrode. Especially capacity of polyaniline electrode at 30CmA discharge rate showed 50% of theoretical specific capacity. However, the energy density *vs.* volume of the PANI cathode is smaller than that of present practical LIB's transition metal oxide cathode such as $LiCoO_2$, $LiMn_2O_4$ etc.. One of the methods to solve this problem is to mix a high density active material such as metal oxide with the polyaniline film. It is reported that the composite electrode consisting of PANI and V_2O_5 exhibits excellent charge and discharge performances.

3. Composite Electrodes

Positive electrode was prepared from a slurry composed of polyaniline and vanadium oxide by the coating method. Polyaniline synthesized by chemical oxidation of aniline is soluble in NMP by reduction using hydrazine monohydrate/ methanol = 5/95 (v/v) . Therefore the soluble polyaniline can be used as a binding material in place of PVdF in cathode electrode. $LiFePO_4$ is investigated as a cathode material for a large scale LIB for electric vehicles, because of its a potential due to low cost, high safety and non-toxicity(5). However, from which electronic conductivity of the pristine $LiFePO_4$ particles is very low with about 10^{-9} Scm^{-1}, usually $LiFePO_4$ are coated with a carbon. Therefore, a soluble polyaniline composite electrodes can be expected to improve the conductivity of $LiFePO_4$(6).

The redox of $LiFePO_4$ takes place at the potential of 3.5 V *vs.* Li/Li^+, which is very similar to the redox potentials of PANI and PPy, and these conducting polymers show good compatibilities with $LiFePO_4$ cathode for LIB.

Fig.1 Reduced PANI synthesized by chemical oxidation

4. Performance of $LiFePO_4$/ PANI composite electrode

$LiFePO_4$ composite cathode was prepared using PANI as a binding material in the same way as V_2O_5 /PANI composite. The composite cathode sheet was prepared as follows. Carbon-coated $LiFePO_4$(C-$LiFePO_4$), acetylene black and PANI were mixed in the weight ratio. The mixed paste was applied onto an aluminium current collector.

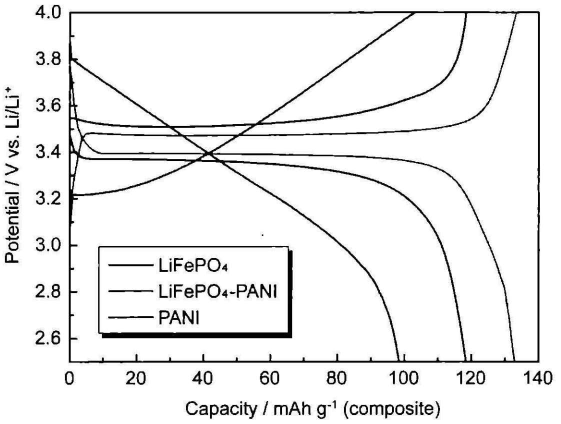


Fig.2　The charge-discharge curves of 5th cycle of [Li metal | 1M LiPF$_6$/EC–DEC) | PANI, LiFePO$_4$–PVdF, or LiFePO$_4$–PANI] cells measured at room temperature.

The charge-discharge measurements for PANI, LiFePO$_4$ -PVdF and LiFePO$_4$-PANI composite electrodes were performed at approximately 1 CmA-rate. The LiFePO$_4$-PVdF electrode showed plateaus at 3.5 V and 3.4 V during the charge and discharge, due to the redox of Fe$^{2+/3+}$ in the olivine framework structure, as expected.

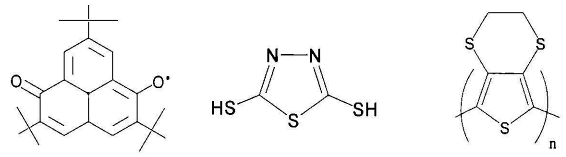
The LiFePO$_4$-PANI composite electrode showed a discharge capacity of 133 mA h g^{-1}, which is larger than that of LiFePO$_4$–PVdF electrode (118mAh g^{-1}). The capacity due to the redox of PANI also contributed to the capacity of the composite electrode.

5.　Advanced Batteries

Using the reaction of organic compounds to stabilize a number of radicals in the molecule , has been proposed high-energy batteries.　A 6-oxophenanthrene(Fig.3(a))(7) has been reported in cell systems involving two-electron reaction. These organic molecules, so it is possible to design a more stable radical sites in one molecule, is an attractive electrode material for batteries.

S. J. Visco, et al(8)., proposed a rechargeable battery system at room temperature by using reversible polymerization reaction of sulfur compound.　The sulfur polymer based on polyacetylene structure deposited by polymerization reaction of carbon disulfide has high theoretical specific energy density of 1675mAh/g.　As for 2,5- dimercapto 1,3,4- thiadiazole (Fig.3(b)) chemical compound which is the organosulfur compound, the reversible change of the monomer and the polymer is possible by the electrochemical redox reaction on PANI electrode.

Recently, a highly dispersed sulfur in mesoporous carbon for the lithium sulfer battery has been reported to show excellent cycling performance with a reversible discharge capacity of about 800mAg^{-1}(9), after 25 cycles.　The lithium polysulfides generated during the charge/discharge process is soluble in the organic liquid electrolyte.　The dissolved polysulfides are able to transfer to the lithium anode by a shuttle mechanism and cause lithium corrosion, which is ascribed to the capacity fading.　Numerous studies focused on diminishing the negative effect of the polysulfides shuttle by retaining the polysulfides at　the cathode region through high surface area adsorbents.　Conductive polymers has been reported as absorption agent and insoluble electrolyte to inhibit shuttle mechanism.　Conducting polymer structure is incorporating some cases of polysulfides.　Energy density of Poly(3,4-ethyrene-dithio) thiophene in Fig.3 (c), has been reported as high as 425mAhg^{-1}(10).　Therefore, sulfur bonds in the conducting polymers are expected to contribute to the electrode reaction.



(a)　　(b)　　(c)

Fig.3　Examples of organic electrode materials of high energy density battery

Battery using the conductive polymer electrodes, the improvement of volumetric energy density (Wh/l) and collector design is an important issue.　New batteries for materials, especially organic batteries, there is a similar challenge. Composite electrode is promising support for technology innovation in lithium-ion batteries has been much anticipated. The near future, the conductive polymer, to be used in practical battery is suitable for manufacturing, development of conductive polymer materials and process technology are required.

6.　References

1),　P.J.Nigrey, D.MacLnnes.Jr., D.P.Navns and A.G.MacDiarmid ; J.Electrochem.Soc., 128, (1981) 1651
2),　T.Nakajima, T.Kawagoe : Synthetic Metals, 28, C629 (1989)
3),　S.Yata, Y.Hato, K.Sakurai, T.Osaki, K.Tanaka and T.Yamabe: Synth.Met.,18, (1987) 645
4),　C. Shmutz et. al., The Electrochem. Soc. Proc., 28, 330-335(1994)
5),　A.K.Padhi, K.S.Nanjundaswamy, J.B.Goodenough, J.Electrochem.Soc.,144 (1997) 1188
6),　T. Tamura et. al.; Chem. Lett. Vol.40, No.8 (2011) 828
7),　T.Sugimoto, Y.Misaki, Y.Arai, Y.Yamamoto, Z.Yoshida, Y.Kai, N.Kasai,　J. AM. Chem. Soc.,110 (1988) 628
8),　S.J. Visco et. al. ; J. Electrochem.Soc., 137 (1990) 750
9),　CAO Yuliang et.al., Phys.Chem. Chem Phys, Vol.13,No.17 (2011) 7660
10), J.Tang, Z.-P. Song, N.Shan, L.-Z.Zhan , J.-Y. Zhang, H.Zhan, Y.H.Zhou, C-H.Zhan, J.Power Sources, 185 (2008) 1434