

Short communication

High energy lithium batteries by molecular wiring and targeting approaches

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Abstract

Three classes of p-type redox active molecules, i.e. triarylamine derivatives, phenothiazine/phenoxazine derivatives, and transition metal complexes are presented in this paper. Their structures, redox potentials and applications for molecular wiring and redox targeting of carbon-free insulating battery materials are discussed in detail.

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1. Introduction

Lithium-ion batteries are the state-of-the-art power sources for portable electronic devices [1]. Lithium insertion materials are preferred over Li-metal, at the expense of energy storage capacity, for reasons of better cycle ability and safety. A notorious problem arises from the poor electronic conductivity of the currently used lithium insertion materials. Thus, the layer-structured LiM^1O_2 ($\text{M}^1 = \text{Co}, \text{Ni}, \text{Mn}, \text{etc.}$), spinel-type $\text{Li}_2\text{Mn}_2\text{O}_4$, $\text{Li}_4\text{Ti}_5\text{O}_{12}$, and the olivine-type LiM^2PO_4 ($\text{M}^2 = \text{Fe}, \text{Mn}, \text{etc.}$) which are typically poor conductors or large band gap semiconductors [2], alone cannot sustain the flow of electric current during the charging and discharging of the battery. Therefore, large quantities of conductive additives have to be used in practical electrode formulations to improve their conductivity, greatly reducing the energy density of the batteries.

We have recently discovered that self-assembled monolayers (SAMs) of redox active molecules on mesoscopic substrates exhibit two-dimensional conductivity if their surface coverage exceeds the percolation threshold [3–5]. Such molecular charge transport layers can be employed to electrochemically address insulating battery materials as shown in Fig. 1(a). The concept of molecular wiring of insulating battery mate-

rials has been successfully demonstrated, where the widely used olivine LiFePO_4 was derivatized with a monolayer of 4-[bis(4-methoxyphenyl)amino]benzylphosphonic acid (**3**) [6]. At equilibrium, the electrochemical potential of the molecular hole transporter is equal to that of the olivine. During charging of the battery a positive polarization is applied to the electrode resulting in the oxidation of the molecule. This moves its redox potential above the Fermi level of the solid, thereby providing the driving force for hole injection from the oxidized molecule into the valence band of olivine. At the same time, Li^+ is ejected. Conversely, during discharging the electron transfer from the current collector into the molecular charge transport film reduces its potential below the Fermi level of the olivine. As a consequence, electrons are injected from an occupied orbital of the molecule into the conduction band of the n-type FePO_4 , and Li^+ is inserted concomitantly.

While intriguing, molecular wiring face stability risks due to possibility of desorption of the redox mediator from the insertion material during the charge and discharge cycle. In addition, the current output is limited by the rate of cross-surface charge percolation and interfacial charge transfer. In order to solve such problems, a new concept of redox targeting by freely diffusing relay molecules to address insulating or poorly conducting lithium insertion materials was proposed [7]. As indicated in Fig. 1(b), the molecular redox shuttle (S) is dissolved in the electrolyte of the cathodic compartment of the cell. During charging S is oxidized at the current collector to S^+ , which delivers the

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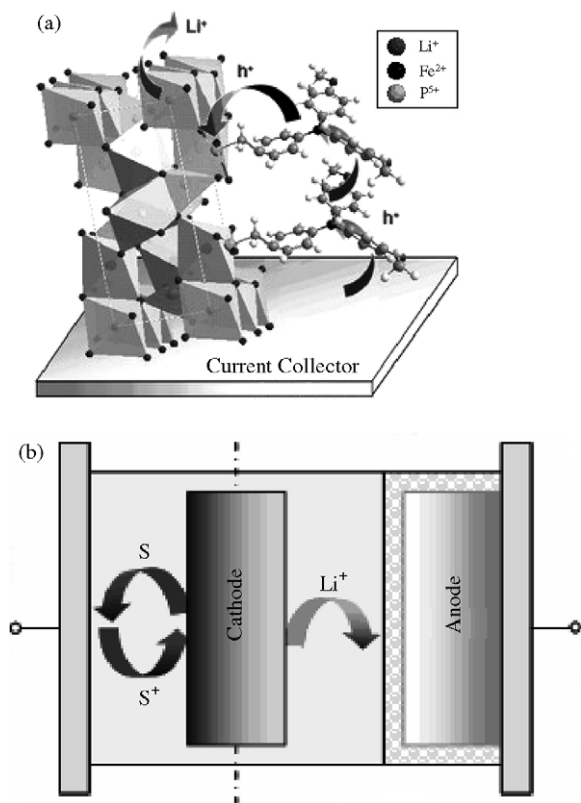


Fig. 1. Schematic model showing the working principle of molecular wiring and redox targeting of insulating battery materials: (a) structure of LiFePO₄ and the surface relay molecule substituted by an alkyl phosphonate anchoring group acting as molecular charge transport material; (b) redox targeting of the olivine material by a freely diffusing molecular shuttle S.

charge to local particles via bulk diffusion. Because the standard redox potential of S⁺ matches closely the Fermi level of olivine, S⁺ will be reduced back to S by hole injection in the LiFePO₄ resulting in the oxidation of Fe(II) to Fe(III) and the release of lithium ions. By contrast, during the discharging process, S⁺ is reduced at current collector to S, which in turn delivers electron to FePO₄. The advantage of using a freely diffusing redox shuttle over molecular wiring is that it allows charge transport to proceed at a much faster rate, enhancing greatly the power output of the battery, even though a special membrane has to be used to block the molecular shuttles from penetrating to the counter electrode compartment.

In this paper, we will present a serial of p-type redox molecules suitable for molecular wiring and redox targeting of insulating cathodic battery materials. By using different substitutes, the potentials can be fine-tuned and these molecules can be used for various cathodic materials for high energy lithium ion batteries.

2. Experimental

2.1. Materials

The molecules studied in this paper have been listed in Table 1. The synthesis and characterization of molecules 1–3, 5, 6, 9, 10 will be published elsewhere, and those of molecules 4, 11–15

have been reported in literatures [3,8,9]. Molecules 7 and 8 were purchased from Acros and used as received.

LiFePO₄ powder was synthesized by a solid state reaction and ball-milled to reduce the particle size [10]. The carbon-free electrode was prepared by mixing the LiFePO₄ powder with 8 wt.% PVDF and stirring with *N*-methyl-2-pyrrolidone (NMP). The resulting homogeneous slurry was then doctor-bladed onto F-doped conducting glass (FTO). After drying in an oven at 100 °C overnight, the films were cut into smaller pieces. The typical thickness of the film was 5–7 μm. The preparation of mesoscopic TiO₂ film has been described in reference [11].

Free molecules 1, 2, 7, 8, 11–13 with different concentrations were dissolved in electrolyte of 1 M LiPF₆/ethylene carbonate (EC) and dimethyl carbonate (DMC) mixture (1:1, w/w). The solutions of the other molecules were prepared in a glove-box by dissolving the compounds in acetonitrile with a concentration of 1 mM. The LiFePO₄ and TiO₂ electrodes were then dipped into the above solution for 3 h. The derivatized electrodes were then rinsed in acetonitrile to remove any weakly adsorbed molecules. The whole process was carried out in an argon-filled glove-box.

3. Electrochemical measurements

Voltammetric measurements employed a PC-controlled AutoLab® PSTA30 electrochemical workstation (Eco Chimie) with counter and reference electrodes of lithium foil. The electrolyte was 1 M LiPF₆/EC + DMC (1:1, w/w).

4. Results and discussion

Despite of their difference in charge transport, where molecular wiring employs cross-surface charge percolation and redox targeting resorts to free diffusion of redox molecules, these two concepts are basically following the same principle of interfacial charge transfer between the redox molecule and the substrate material. In order to achieve fast charge transfer rate and consequently larger current output, these redox molecules should possess strong electronic coupling with the electrode material and low reorganization energy. Furthermore, in order to be able to withdraw electrons from the cathodic material during the charging step and return them during the discharging step, its redox potential is required to closely match the Fermi level of the battery material.

Table 1 lists three classes of p-type redox active molecules, i.e. triarylamine derivatives, phenothiazine/phenoxazine derivatives, and transition metal complexes. Following, their structures, redox potentials and their potential applications for redox targeting and molecular wiring of insulating battery materials will be presented in detail, where the free molecules will be discussed for redox targeting concept, while the other molecules with phosphonic or carboxylic acid anchoring groups for molecular wiring concept.

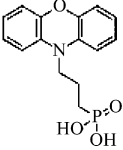
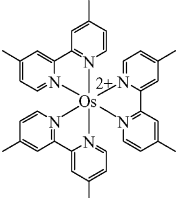
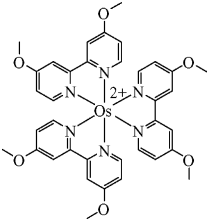
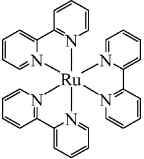
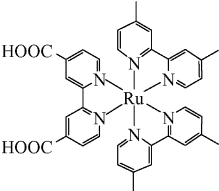
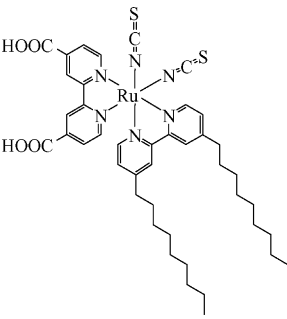
4.1. Triarylamine derivatives (1–6)

Triarylamine derivatives are well known as p-type organic semiconductor, and are widely used as hole transporting materi-

Table 1
Structure and oxidation potential of the redox active molecules used for molecular wiring and redox targeting

Molecule	Structure	E_{ox1} (V, vs. Li^+/Li)	E_{ox2} (V, vs. Li^+/Li)
1		3.95	
2		4.55	
3		3.46	
4		3.42	4.05
5		3.79	
6		3.05	3.37
7		3.46	
8		3.48	4.36
9		3.45	

Table 1 (Continued)

Molecule	Structure	E_{ox1} (V, vs. Li^+/Li)	E_{ox2} (V, vs. Li^+/Li)
10		3.45	
11		3.53	
12		3.32	
13		4.18	
14		4.10	
15		3.55	

als in organic transistor, light-emission diode, and photovoltaic devices, etc. [12–14]. The electrochemistry of triarylamine derivatives has been extensively investigated. Upon positive polarization, it undergoes stepwise two $1e^-$ oxidations, and forms stable radical cation and dication. As the molecule 1–6 shown in Table 1, by using different electron donating or withdrawing substitutes, the first oxidation potential of triarylamine can be tuned between 3.00 and 4.50 V (versus Li^+/Li), which is well located in the potential range of con-

ventional cathodic materials for lithium ion batteries. As these molecules are adsorbed on the surface of insulating mesoscopic metal oxide, it shows fast lateral cross-surface hole percolation through the assembled molecular monolayer [3,4]. 4-[bis(4-methoxyphenyl)amino]benzylphosphonic acid (3) has an oxidation potential of 3.46 V, being very close to that of LiFePO_4 . A significant improvement of the electrochemical performance of LiFePO_4 has been observed upon wired with 3 [6].

4.2. Phenothiazine and phenoxazine derivatives (7–10)

Similar to triarylamine, phenothiazine and phenoxazine derivatives also form stable radical cation and dication during stepwise $1e^-$ oxidation. The formed radicals are well stabilized by the charge delocalization within the conjugated ring structure. As the CV (red curve) indicated in Fig. 2, 10-methylphenoxazine (**8**) shows a reversible $1e^-$ oxidation wave at ~ 3.48 V and a second less reversible oxidation wave at ~ 4.36 V in 1 M $\text{LiPF}_6/\text{EC} + \text{DMC}$ (1:1) electrolyte at a scan rate of 0.1 V s^{-1} . 10-methylphenothiazine (**7**) has a very similar behavior, the first oxidation potential being slightly higher than that of LiFePO_4 . In contrast, as carbon-free LiFePO_4 was used as working electrode, instead of the normal peaks, the CVs of both compounds display the behavior of typical catalytic waves, the appearance of current plateaus reflecting sustained oxidation and reduction processes due to molecular redox targeting.

As a result of strong electronic coupling between adjacent anchored molecules and low reorganization energy, phenothiazine and phenoxazine derivatives with phosphonic acid anchoring group also show efficient cross-surface hole percolation as assembled on mesoscopic oxide film. Fig. 3(a) shows the CVs of molecule **10** adsorbed on mesoscopic TiO_2 . Despite the insulating nature of the mesoscopic electrode a chemically reversible anodic wave appears at ~ 3.45 V (versus Li^+/Li) indicating occurrence of $1e^-$ oxidation by efficient cross-surface hole percolation. Intriguingly, since its potential is very identical to that of LiFePO_4 , as the molecule was adsorbed on carbon-free LiFePO_4 electrode, fast cross-surface hole percolation followed by interfacial charge injection renders sustained oxidation and reduction currents during cyclic voltammetric measurement. Very similar to the triarylamine derivative (**3**), two well-defined current plateaus were also observed, indicating that LiFePO_4 being electrochemically addressed via cross-surface conduction through the electro-active molecular layer.

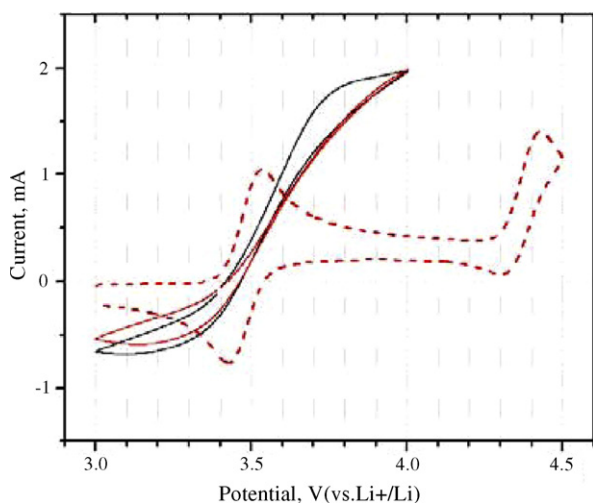


Fig. 2. Cyclic voltammograms of Pt disk (dash line) and carbon-free $\text{LiFePO}_4/\text{FTO}$ electrodes (solid line) in 1 M $\text{LiPF}_6/\text{EC} + \text{DMC}$ (1:1) electrolyte in the presence of 90 mM **7** (black) and **8** (red). The scan rate is 0.1 V s^{-1} .

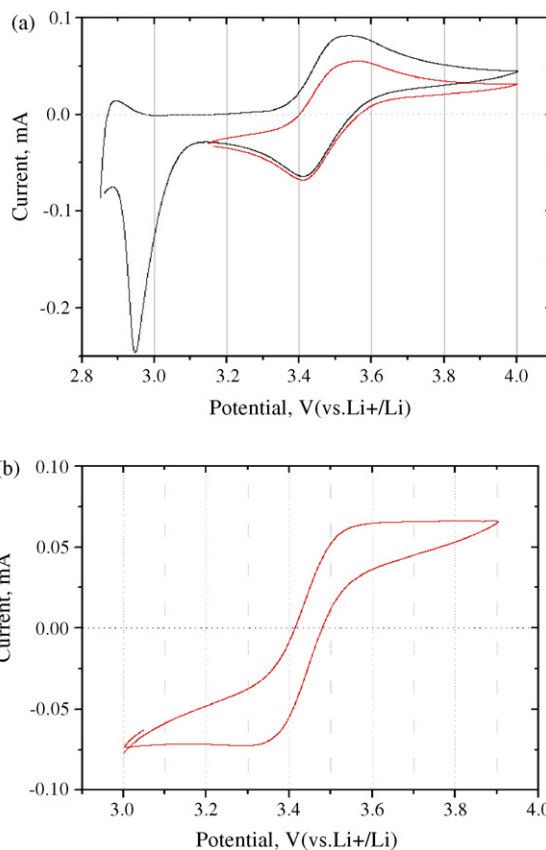


Fig. 3. Cyclic voltammograms of molecule **10** adsorbed on (a) mesoscopic TiO_2 film, the electrolyte being 1 M $\text{LiPF}_6/\text{EC} + \text{DMC}$ (1:1); (b) $\text{LiFePO}_4/\text{FTO}$ electrode, the electrolyte being saturated $\text{LiPF}_6/\text{EC} + \text{DMC}$ (1:1). The scan rate is 0.1 V s^{-1} .

4.3. Transition metal complexes (11–15)

Ruthenium/osmium polypyridyl complexes have been widely employed as stable and reversible mediators in electrochemical devices and optoelectronic systems [8,15–17]. By changing the ligand property, the redox potential can be readily tuned. $\text{Os}(\text{mbpy})_3^{2+}$ (**11**) and $\text{Os}(\text{mobpy})_3^{2+}$ (**12**) with the potentials of 3.53 and 3.32 V, respectively, just straddle that of LiFePO_4 and have been successfully used to target the carbon-free olivine electrode [7]. Ruthenium complexes have much higher potential as indicated in Table 1. For instance, $\text{Ru}(\text{mbpy})_3^{2+}$ (**13**) has an oxidation potential of 4.18 V, which is a promising candidate for LiMnPO_4 targeting. It has been shown in our previous paper that, NCS-ligands of heteroleptic ruthenium complexes play a pivotal role in greatly accelerating the rate of cross-surface hole transfer as the complexes were anchored on the surface of mesoscopic metal oxide [5]. Complex **15** has two carboxylic acid anchoring groups, which can be tightly bonded on the surface of battery materials. The effective orbital overlapping of NCS groups between neighbouring molecules makes it good candidate for molecular wiring. The potential of **15** in battery electrolyte is determined to be ~ 3.55 V (versus Li^+/Li). When this molecule is adsorbed on LiFePO_4 , it shows efficient hole injection and Li^+ extraction upon charging.

5. Conclusion

The structures, oxidation potentials and other electrochemical properties of triarylamine derivatives, phenothiazine/phenoxazine derivatives and transition metal complexes are presented in this study. All molecules show stable and reversible redox behavior upon polarization. By using proper substituents, these molecules can be used as promising mediators for redox targeting of insulating battery materials. Alternatively, these molecules can be assembled on the surface of battery materials in the presence of anchoring groups. Fast cross-surface hole percolation followed by interfacial charge injection affords reversible charging and discharging of the battery materials. It is expected that the space occupied by the electrolyte mediator or the molecular charge transport layer is negligibly small. Thus the volume of conductive additive is greatly reduced opening up the possibility for a much improved energy storage density of lithium battery.

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References

- [1] J.-M. Tarascon, M. Armand, *Nature* 414 (2001) 359.
- [2] M.S. Whittingham, *Chem. Rev.* 104 (2004) 4271.
- [3] P. Bonhôte, E. Gogniat, S. Tingry, C. Barbé, N. Vlachopoulos, F. Lenzmann, P. Comte, M. Grätzel, *J. Phys. Chem. B* 102 (1998) 1498.
- [4] Q. Wang, S.M. Zakeeruddin, J. Cremer, P. Bäuerle, R. Humphry-Baker, M. Grätzel, *J. Am. Chem. Soc.* 127 (2005) 5706.
- [5] Q. Wang, S.M. Zakeeruddin, Md. K. Nazeeruddin, R. Humphry-Baker, M. Grätzel, *J. Am. Chem. Soc.* 128 (2006) 4446.
- [6] Q. Wang, N. Evans, S.M. Zakeeruddin, I. Exnar, M. Grätzel, *J. Am. Chem. Soc.* 129 (11) (2007) 3163.
- [7] Q. Wang, S.M. Zakeeruddin, D. Wang, I. Exnar, M. Grätzel, *Angew. Chem. Int. Ed.* 45 (48) (2006) 8197.
- [8] S.M. Zakeeruddin, D.M. Fraser, Md.K. Nazeeruddin, M. Grätzel, *J. Electroanal. Chem.* 337 (1992) 253.
- [9] S.M. Zakeeruddin, Md.K. Nazeeruddin, R. Humphry-Baker, P. Péchy, P. Quagliotto, C. Barolo, G. Viscardi, M. Grätzel, *Langmuir* 18 (2002) 952.
- [10] D. Wang, L. Hong, Z.X. Wang, X.D. Wu, Y.C. Sun, X.J. Huang, L.Q. Chen, *J. Solid State Chem.* 177 (2004) 4582.
- [11] C.J. Barbe, F. Arendse, P. Comte, M. Jirousek, F. Lenzmann, V. Shklover, M. Grätzel, *J. Am. Ceram. Soc.* 80 (1997) 3157.
- [12] U. Bach, D. Lupo, P. Comte, J.-E. Moser, F. Weissörtel, J. Salbeck, H. Spreitzer, M. Grätzel, *Nature* 395 (1998) 583.
- [13] Y. Shirota, *J. Mater. Chem.* 10 (2000) 1.
- [14] M. Thelakkat, *Macromol. Mater. Eng.* 287 (2002) 442.
- [15] A. Juris, V. Balzani, *Coord. Chem. Rev.* 84 (1988) 85.
- [16] B. O'regan, M. Grätzel, *Nature* 353 (1991) 737.
- [17] A. Heller, *J. Phys. Chem.* 96 (1992) 3579.