

Polypyridine complexes of iron used as redox shuttles for overcharge protection of secondary lithium batteries

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Abstract

The 2,2'-bipyridyl and 1,10-phenanthroline complexes of iron, which show oxidation potential ~ 0.7 V more positive than that of ferrocene, were studied for their possible use as redox shuttles for the overcharge protection of secondary lithium batteries. The shuttle voltage was found to be around 3.8–3.9 V. The electrochemical stability of these complexes at the electrodes of lithium batteries was also investigated.

Keywords: Secondary lithium batteries; Polypyridine; Iron; Redox shuttles

1. Introduction

The voltage of secondary batteries of the aqueous electrolyte-type is limited to ~ 2.0 V by the decomposition voltage of the solvent (water). At the same time, the overcharge protection of both cathode and anode of these types of secondary battery can be easily provided by the decomposition of water at one electrode and the recombination of the gaseous product at the other electrode, as in sealed lead/acid, Ni–Cd and Ni–metal hydride batteries.

On the other hand, organic solvents used in many secondary Li batteries are in general not capable of being reversibly oxidized or reduced, so measures must be taken in order to avoid harmful effects of overcharge, such as decomposition of organic solvents and deterioration of electrode materials.

The addition of ferrocene and its derivatives has been suggested as possible means of internal overcharge protection for secondary Li batteries [1–3]. The ferrocenes are easily available and relatively inexpensive, and their solubility and stability are fairly good in most of the organic solvents commonly used in Li batteries. However, the oxidation potential of this type of compounds (usually 3.0–3.5 V versus Li/Li⁺) has been found to be not sufficiently positive. The shuttle mechanism can thus start to operate before the complete charge of the electroactive materials, as indicated by lowering the capacity of the charged cell [1].

We have recently probed the possibility of using polypyridine complexes of Fe(II) as redox shuttles in

secondary Li batteries. In this paper the preliminary results of our experimental studies are presented.

2. Experimental

The tris(2,2'-bipyridyl) and tris(1,10-phenanthroline) complexes were synthesized according to Refs. [4,5]. All organic solvents were purified and dried using standard procedures. The positive electrode materials λ -MnO₂, spinel Li_xMn₂O₄ and Bi₂O₃-doped composite dimensional MnO₂(CDMO) were synthesized in our laboratory [6–8]. Petroleum coke used in this experiment was heat-treated at ~ 1600 °C.

The electrochemical behaviour of the polypyridine complexes was studied with cyclic voltammetry (CV) at a platinum microdisc electrode (diameter = 100 μ m). Their behaviour at the positive and negative electrodes of secondary Li batteries was studied with the powder microelectrode technique [9] or in experimental Li cells. Ag/AgCl electrode placed directly in the electrolyte was used as reference electrode. In (1:1)propylene carbonate–dimethoxyethane (PC–DME) + 1 M LiClO₄, its potential is +3.0 V versus the Li/Li⁺ electrode.

3. Results and discussion

The CVs of Fe(bpy)₃(ClO₄)₂ and Fe(phen)₃(ClO₄)₂ in (1:1)PC–DME measured with the platinum microelectrode are depicted in Fig. 1. Ferrocene was added

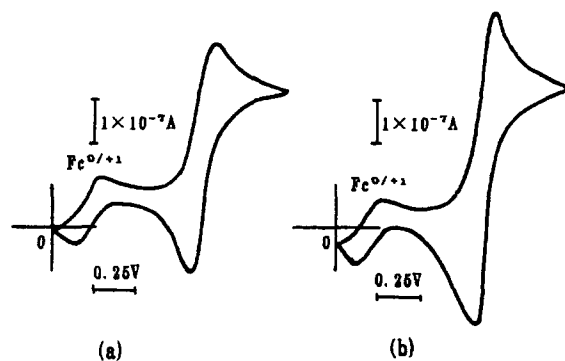


Fig. 1. Cyclic voltammograms obtained in (1:1)PC-DME + 1 M LiClO₄ solutions saturated with (a) Fe(bpy)₃(ClO₄)₂, and (b) Fe(phen)₃(ClO₄)₂; $v = 100$ mV/s, ferrocene added as potential marker.

Table 1
Summary of electrochemical potentials

Redox system	E^0 (V)	E_{pa} (V vs Ag/AgCl)	ΔE_{pa} (V)
Fe(bpy) ₃ (2+/3+)	1.11	0.95	0.65
Fe(phen) ₃ (2+/3+)	1.13	1.00	0.70
Ferrocene (0/1+)	0.40	0.30	

to the solution as a potential marker to show the differences between oxidation potentials of the polypyridine and ferrocene complexes. In Table 1, the formal redox potentials in aqueous system (E^0), the anodic peak potential (E_{pa}) and the difference between the anodic peak potentials of the Fe(II)L₃ complex and that of ferrocene (ΔE_{pa}) in PC-DME electrolyte are listed.

Both polypyridine complexes show E_{pa} around 3.9–4.0 V versus Li/Li⁺, i.e., 0.65–0.70 V more positive than the ferrocene couple. Fe(bpy)₃²⁺ and Fe(phen)₃²⁺ salts are moderately soluble in (1:1)PC-DME (about 0.05 to 0.1 M at room temperature).

One of the problems associated with the use of transition metal ion polypyridine complexes as redox shuttle for overcharge protection of Li batteries is the possibility of legend-based reduction of these complexes at the negative electrode. Fig. 2 shows the different behaviours of Fe(bpy)₃²⁺ and ferrocene in acetonitrile (AN), measured with a platinum microelectrode scanned at 200 mV/s. The ferrocene gives no reduction peak up to -2.0 V versus Ag/AgCl, while the Fe(bpy)₃²⁺ gives rise to a series of reduction-oxidation peaks (2+/1+, 1+/0, and 0/-1) in the potential range from -1.0 to -2.0 V. If similar reduction can take place also in Li batteries, the charged battery will self-discharge quickly as a result of internal short circuit due to the cyclic reduction-oxidation of the redox shuttle.

Nevertheless, our experimental results seem to indicate that the legend-based reduction of the Fe(II) complex at the negative electrode can be effectively

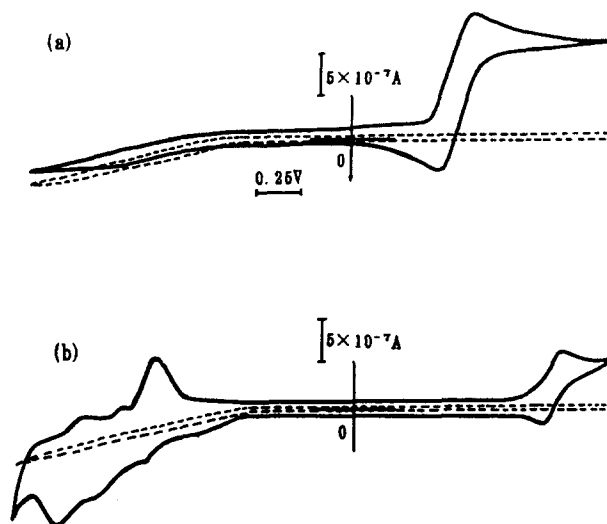


Fig. 2. Comparison of the electrochemical behaviour of ferrocene and Fe(bpy)₃(ClO₄)₂ in AN + 0.2 M (Bu)₄NPF₆: (a) ferrocene, 5 mg/ml, and (b) Fe(bpy)₃(ClO₄)₂, 10 mg/ml.

hampered by the passivation of the electrode surface. Aurbach and co-workers [10–13] have shown that both Li and non-active electrodes (Pt, Au, C, Ag, Ni, etc.) are covered with films formed by the precipitation of species which are the reduction products between electrodes and the polar aprotic solvents (e.g., PC, ethylene carbonate, DME, tetrahydrofuran, γ -butyrolactone). In Fig. 3, the electrochemical behaviour of Fe(bpy)₃²⁺ and Fe(phen)₃²⁺ in a wide potential range at the platinum microelectrode are depicted. When the rate of the potential scan is high (≥ 100 – 200 mV/s), some electrochemical events are faintly visible in the range from -1 to -2 V. It is still not certain whether these signals come from the solvent or from the redox couple. At a lower scan rate these signals diminish significantly, probably due to more complete passivation of the electrode surface. By comparing Figs. 2 and 3 it is clear that the rate of legend-based reduction of the polypyridine complexes is much less in PC-DME than in AN. The behaviours of the complexes at the negative electrode were studied with the powder microelectrode technique. The microelectrode (diameter = 100 μ m) was packed with fine petroleum coke powder, which can be reversibly lithiated electrochemically in a LiClO₄ solution in PC-DME, as indicated by the shape of the CV in the far-negative potential range (Fig. 4). If Fe(bpy)₃²⁺ could be reduced at the lithiated carbon electrode, anodic peak due to the re-oxidation of the reduced complex should be visible on the curve recorded during the reversed scan (anodic scan). The fact that CV does not change upon addition of Fe(bpy)₃²⁺, as shown in Fig. 4, indicates that no significant legend-based reduction takes place at the negative electrode.

The behaviours of the polypyridine complexes at the positive electrode were also studied with the powder

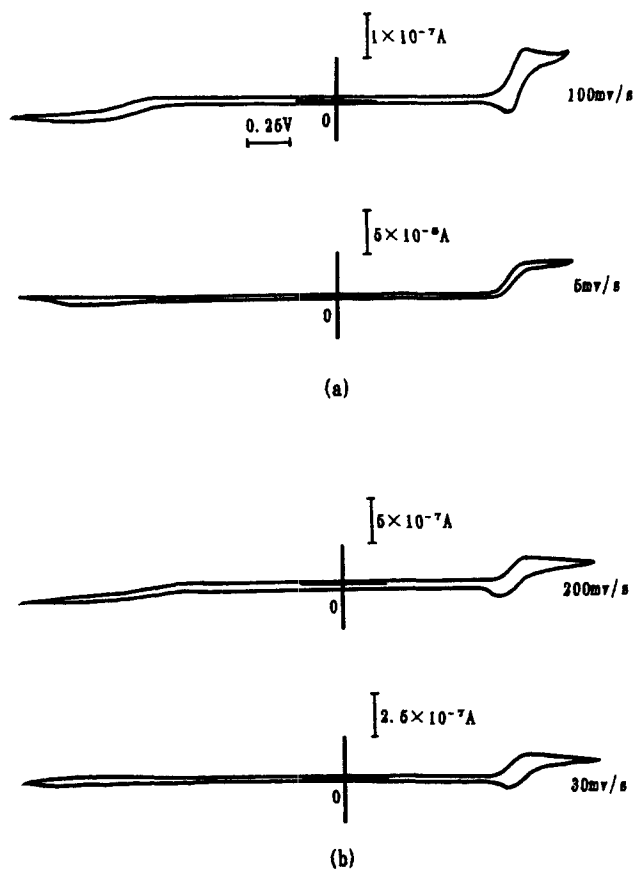


Fig. 3. Cyclic voltammograms measured in (1:1)PC-DME+1 M LiClO₄ solution containing: (a) Fe(bpy)₃(ClO₄)₂, 5 mg/ml, and (b) Fe(phen)₃(ClO₄)₂, 20 mg/ml.

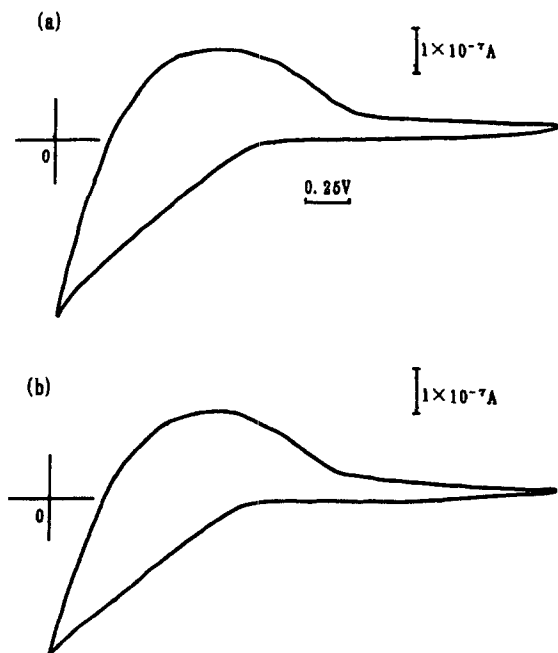


Fig. 4. Cyclic voltammograms measured with the petroleum coke powder packed microelectrode in (1:1)PC-DME + 1 M LiClO₄: (a) before, and (b) after addition of Fe(bpy)₃(ClO₄)₂, 5 mg/ml, $v=5$ mV/s, electrode potential vs. Li/Li⁺.

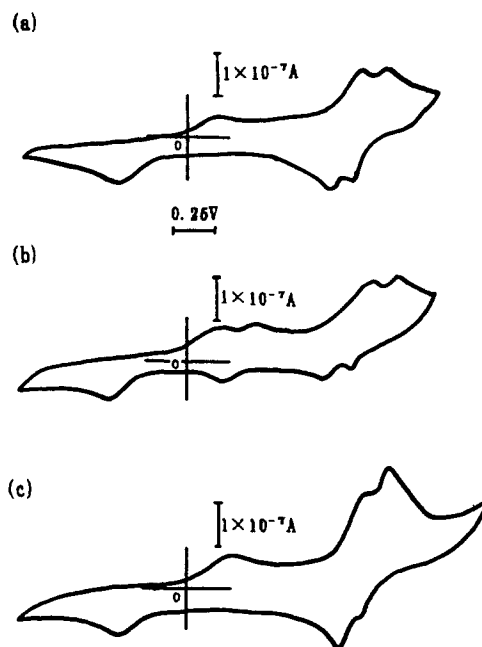


Fig. 5. Cyclic voltammograms measured with powder microelectrode packed with λ -MnO₂ in (1:1) PC-DME + 1 M LiClO₄: (a) no addition; (b) 5 mg/ml ferrocene, and (c) 20 mg/ml Fe(phen)₃(ClO₄)₂; $v=5$ mV/s.

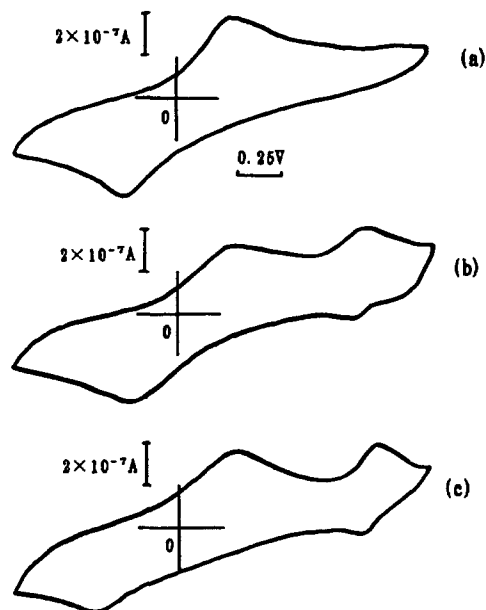


Fig. 6. Cyclic voltammograms measured with powder microelectrode packed with CDMO in (1:1) PC-DME + 1 M LiClO₄: (a) no addition; (b) 10 mg/ml Fe(bpy)₃(ClO₄)₂, and (c) 10 mg/ml Fe(phen)₃(ClO₄)₂; $v=5$ mV/s.

microelectrodes. In such studies the microelectrodes were packed with the positive electrode material powders (λ -MnO₂, CDMO and spinel Li_xMn₂O₄ mixed with petroleum coke powder). CVs of λ -MnO₂ measured in blank (LiClO₄ in PC-DME) solution and after addition of ferrocene or Fe(phen)₃²⁺ are presented in Fig. 5. Microelectrodes packed with spinel Li_xMn₂O₄ gave CVs

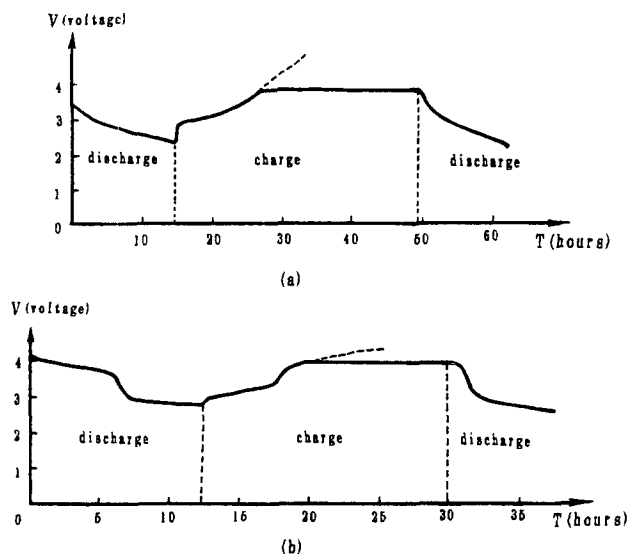


Fig. 7. Charge/discharge curves of experimental (a) Li(C)/(1:1)PC-DME + 1 M LiClO₄/CDMO, and (b) Li(C)/(1:1)PC-DME + 1 M LiClO₄/spinel Li_xMn₂O₄ cells containing 20 mg/ml Fe(bpy)₃²⁺(ClO₄)₂; $I = 0.5 \text{ mA/cm}^2$ (10 mA/g) for both charge and discharge.

very similar to those shown in Fig. 5. The presence of ferrocene in the electrolyte gives rise to a pair of redox peaks in the range from 0.2 to 0.3 V, which is far more negative than the potential range of the second stage charging of λ -MnO₂ (0.9–1.2 V). On the other hand, the oxidation peak of Fe(phen)₃²⁺ almost coincides with the last stage charging of λ -MnO₂. Fig. 6 shows that the charging of CDMO takes place in the potential range more negative than that of λ -MnO₂, and the oxidation peaks of both Fe(bpy)₃²⁺ and Fe(phen)₃²⁺ appear in the potential range corresponding to almost completion of charging of the electrode materials.

Fig. 7 shows the effects of the addition of Fe(bpy)₃(ClO₄)₂ (20 mg/ml) on the charge/discharge characteristics of experimental Li cells using spinel Li_xMn₂O₄ and CDMO as positive electrode materials. The dotted lines indicate overcharge voltage in the

absence of redox shuttle. In the presence of Fe(bpy)₃²⁺, the cell overcharge was found to be limited to 3.85–3.95 V. The charging of CDMO takes place mainly below 3.9 V (see Fig. 6), so the capacity of the cell is only slightly affected (Fig. 7(a)). On the other hand, the second stage of charging of the spinel Li_xMn₂O₄ takes place in the voltage range from 3.8 to 4.3 V, so upon addition of Fe(bpy)₃²⁺ the depth of the second stage charging is limited to about 20% (Fig. 7(b)). Therefore, the development of redox shuttle capable of limiting cell voltage to 4.2–4.3 V is highly preferred for the overcharge protection of the so-called 4 V Li cells.

The long-term stability of these complexes in practical Li cells and their effects on the capacity and self-discharge rate of these cells are under investigation in our laboratory.

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