Electrochemical and X-ray photospectroscopy studies of polytetrafluoroethylene and polyvinylidene fluoride in Li/C batteries

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Abstract

The stability of polytetrafluorethylene (PTFE) and polyvinylidene fluoride (PVDF) used as the anode binders in lithium-ion batteries was studied by electrochemical and X-ray photospectroscopy (XPS) measurements. The characteristic discharge/charge curves for PTFE and PVDF were obtained. It is shown that the behavior of PTFE and PVDF exhibits much discrepancy when they are attacked by high active lithium ion in electrochemical cells. PTFE reacts with lithium easily and decomposes during the first discharge process, which is indicated by a long plateau appearing around 1.2 V in the first discharge curve of Li/Ni(PTFE) cell. XPS results show that PTFE decomposes after one discharge/charge cycle. PVDF is rather stable due to a possible surface passivation process. © 1997 Elsevier Science S.A.

1. Introduction

During the last decade, lithium-ion batteries are being intensively studied. Great efforts have been made to improve their capacity and cycle life. In the lithium-ion battery, the cathode which contains $LiCoO_2$, $LiNiO_2$ or $LiMnO_2$ is the lithium sources. During the first charge process, lithium ions de-intercalated from the cathode were intercalated into the anode which contains carbonaceous materials. Lithium ions are shifted between the two electrodes during the charge/discharge process. It should be mentioned that lithium ions moved to the anode during the first charge cannot be fully removed to the cathode at discharge. It causes the first cycle capacity loss. This capacity loss can be 50% in some cases. Reducing this capacity loss is crucial for enhancing the capacity of batteries. Some researchers supposed that this capacity loss was mainly due to the decomposition of the electrolyte and the formation of a passivation layer (SEI) on the carbon surface [1,2]. Li [3] investigated PTFE as an anode binder and realized that the decomposition of the anode binder attacked by high active lithium might contribute also to this capacity loss. Via X-ray diffraction (XRD) and electrochemical measurements, he found that a plateau at about 0.8 V in the discharge curve of an Li/C laboratory testing cell was caused by the reaction between active lithium ions and the PTFE binder.

In this work, the mechanism of the decomposition of PTFE was studied by electrochemical and XPS measurement. Because F is assumed to contribute to the electrochemical reduction of PTFE, attention is also paid to another commonly used binder, PVDF, which contains also F. In the case of carbon electrode, lithium ions can be intercalated into the carbon lattice; it is not easy to distinguish this process and the possible decomposition of the binder during discharging. In order to avoid this complexity, nickel powder was mixed with the PTFE and PVDF binders to act as the working electrodes.

2. Experimental

13 wt.% of PTFE and PVDF were mixed with nickel powder. The mixture was pressed into pellets with diameter of 10 mm under pressure of 10 kg/cm^2. The weight of the pellets was around 20 mg. Electrochemical testing cell was constructed with the pellets as the cathode, lithium foil as the anode, Celgard 2400 as the separator, and 1 M $LiPF_6$ in EC:DEC (1:1) as the electrolyte. An Li/Ni cell was also constructed for comparison. Discharge/charge cycling was done by self-made PC-controlled battery testing system. The

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initial open-circuit voltage is about 3 V. The cells were first discharged to 0 V at certain constant current densities, then the cells were charged to 2 V. After this first discharge/charge cycle, the pellets were taken out from the cells, washed with diethyl carbonate (DEC), and dried in vacuum. XPS measurements were carried out using X-ray photospectrometer from VG Company (UK) with Al X-ray radiation. Another binder without F atoms was also studied accordingly for comparison.

3. Results and discussion

Fig. 1 shows the first discharge curves of Li/Ni(PTFE) and Li/Ni(PVDF) cells at a very low current density, 12.5 $\mu A/cm^2$. The specific capacity was calculated according to the weight of the electrode. A long plateau at ~ 1.2 V appears in the discharge curve for the Li/Ni(PTFE) cell, and the total capacity reaches 128 mAh/g. As for the Li/Ni(PVDF) cell, two short plateaus appear at ~ 1.3 and ~ 0.8 V, and its total capacity is only 18 mAh/g. It is obvious that the binder plays an important role for this difference. If we attribute the additional discharge capacity of the Li/Ni(PTFE) cell to the reaction of lithium ions with PTFE, the capacity contributed by PTFE is 846 mAh/g.

Fig. 2 shows the first discharge/charge curves of Li/Ni(PTFE), Li/Ni(PVDF) and Li/Ni cells at 0.125 and 0.25 mA/cm². At higher current densities, the voltages of the plateaus are lowered and their capacities decrease. This is due to the high polarization under large current densities. In the case of the Li/Ni(PTFE) cell, the fast drop of voltage is attributed to a high electrode polarization and the following activation process. Li/Ni(PVDF) and Li/Ni cells show similar discharge curves. The two plateaus of the Li/Ni cell may be attributed to lithium intercalation into the surface oxide layer of nickel and the decomposition of the electrolyte upon nickel or the nickel oxide surface. The discharge capacity of Li/Ni(PVDF) is smaller than that of the Li/Ni cell because it contains only 87% Ni. By analyzing the discharge curve of Li/Ni(PVDF) and Li/Ni, there is no observeable extra capacity contributed by PVDF. Therefore, no obvious evi-
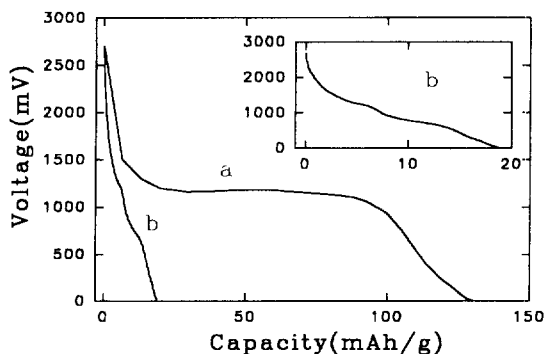
dence of the electrochemical reduction of PVDF can be found in this experiment.

After the cells had been cycled once at 0.125 mA/cm², Ni(PVDF) and Ni(PTFE) electrode pellets were studied by XPS. To make a comparison, XPS of pure PTFE and PVDF powders were measured also. Fig. 3 shows their F(1s) spec-
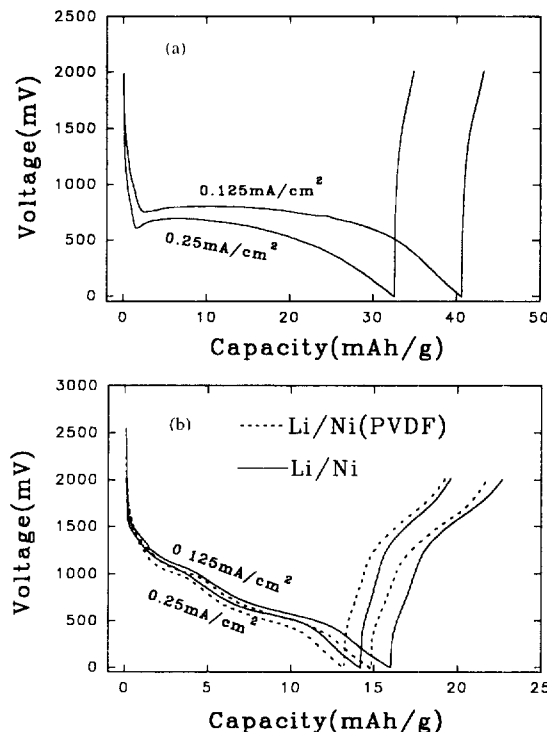

Fig. 2 Discharge/charge curves of electrochemical cells at 0.125 and 0.25 mA/cm²: (a) Li/Ni(PTFE) cell, and (b) Li/Ni(PVDF) and Li/Ni cells

Fig. 1. The discharge curves of electrochemical cells at 12.5 μA/cm²: (a) Li/Ni(PTFE) cell, and (b) Li/Ni(PVDF) cell.
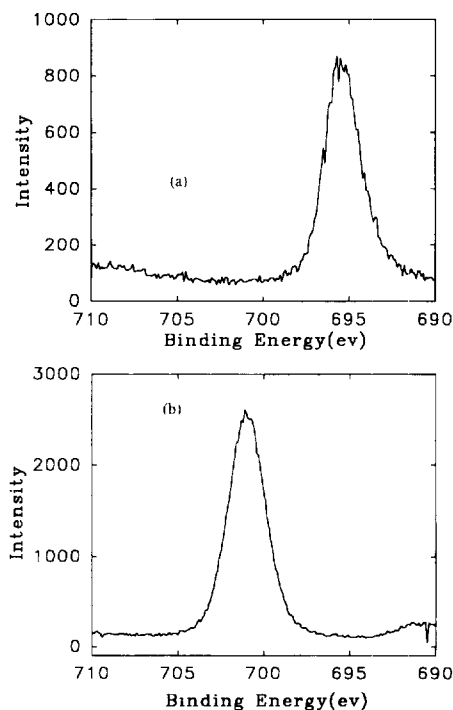

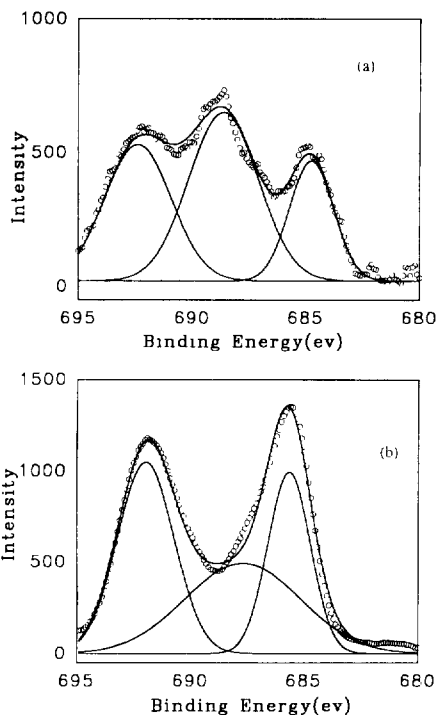Fig. 3. XPS F(1s) spectra of pure (a) PTFE and (b) PVDF powders.

Fig. 4. F(1s) spectra of Ni(PTFE) sample (a) before and (b) after discharge/charge cycling
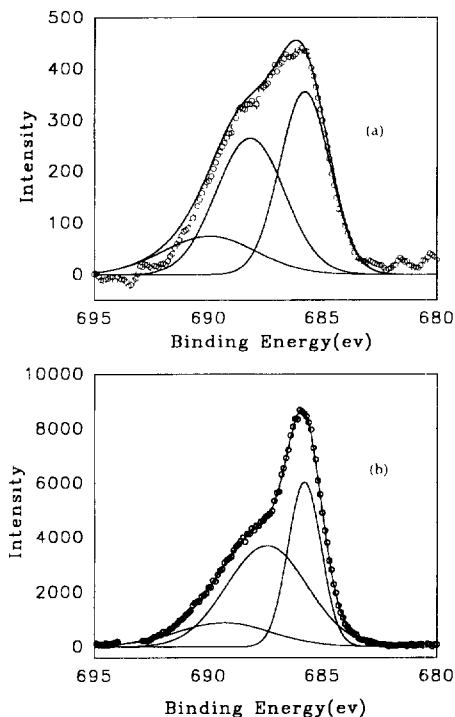

Fig 5. F(1s) spectra of Ni(PVDF) sample (a) before and (b) after discharge/charge cycling.

tra. A single peak appears for both samples. It should be mentioned that the peaks may shift due to the low conductivity of the samples [4]. Figs. 4 and 5 present F(1s) spectra of Ni(PTFE) and Ni(PVDF) samples. The peaks were fitted by a Gaussian function. Three peaks can be separated for both

pristine samples. It is still not fully understood why three peaks appear in this range. We assume that the peak at 688–689 eV can be assigned to the normal F(1s) spectra of PTFE and PVDF according to Ref. [4]. The low energy peak can be attributed to the formation of partial Ni–F bands, some charges are transferred from Ni atoms to F atoms, and screening effects become intensified, so the peaks shift to the lower binding energy. Whether the peak appearing in the Ni(PTFE) spectra at 692 eV can be attributed to the interaction between F–F atoms is still an open question. After the electrochemical cycling, not only the relative intensities but the positions of the peaks change. In the case of Ni(PTFE), the intensity of the normal F(1s) peak decreases remarkably and its position shifts to lower energy. It indicates that there are obvious changes in the form of the polymer during this process. As for Ni(PVDF), the changes are much smaller. In order to clarify if LiPF$_6$ which contains F contributes to this change, F(1s) spectrum of the Ni pellet containing binder without F atoms after the first discharge/charge cycle was measured, see Fig. 6. Because of the low concentration of F atoms, the signal was very weak. This spectrum was obtained by scanning twenty times. Therefore, it indicates that LiPF$_6$ in the electrolyte has no obvious effects on the change of F(1s) spectra in Figs. 4 and 5.

We may assume that PTFE can be reduced electrochemically according to the following reaction

$$(C_2F_4)_n + 4nLi^+ + 4ne^-$$

$$\rightarrow 2nC \text{ (amorphous carbon)} + 4nLiF \qquad (1)$$
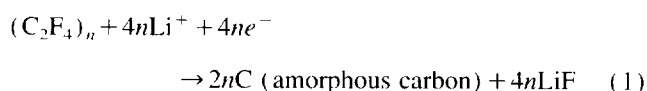
It is plausible to assume that the carbon is in an amorphous state because graphitization process does not happen at room temperature. The theoretical capacity of PTFE is 1072 mAh/g. In this work, an additional capacity of 846 mAh/g was obtained when the discharge current density is 12.5 μA/cm^2. It means that most of the PTFE can be decomposed in this case. At the beginning, the surface is reduced. The reduction product is carbon and LiF. Because carbon is a good electronic conductor and LiF is a good ion conductor, the reaction can go inward. As for the Ni(PVDF) sample, F on the surface may be taken away according to
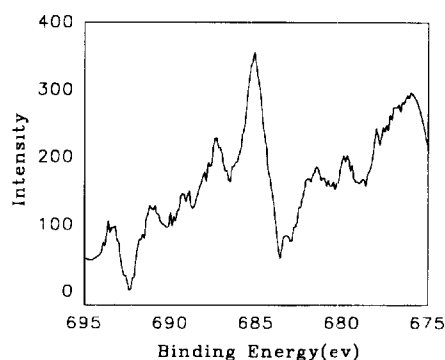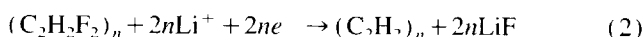
$$(C_2H_2F_2)_n + 2nLi^+ + 2ne \rightarrow (C_2H_2)_n + 2nLiF \qquad (2)$$

Fig. 6 F(1s) spectrum of Ni (non-fluorine binder) sample after discharge/charge cycling.

Because the reaction product $(C_2H_2)_n$ is an insulator, it hinders the further reaction to proceed; this reduction can happen only on the surface. It is a surface passivation process. This assumption is consistent with the experimental results that the intensity and position of the F(1s) spectra change after cycling but no obvious extra capacity are obtained. Therefore, we can conclude that PVDF is much more stable than PTFE as an anode binder in lithium-ion batteries due to a surface passivation effect.

4. Conclusions

PTFE and PVDF are commonly-used binders in lithium-ion batteries. After studying their stability as the anode binders in lithium-ion batteries by analyzing discharge curves of Li/Ni(PTFE), Li/Ni(PVDF) and Li/Ni, and XPS spectra before and after electrochemical cycling, we note that PTFE can easily be reduced electrochemically during the lithium intercalation process but PVDF is much more stable due to a surface passivation effect.

Acknowledgements

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