

Study of poly(acrylonitrile-methyl methacrylate) as binder for graphite anode and LiMn_2O_4 cathode of Li-ion batteries

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Abstract

We evaluated poly(acrylonitrile-methyl methacrylate) (AMMA, AN/MMA = 94:6) as a binder for the graphite anode and the LiMn_2O_4 cathode of Li-ion batteries by studying the cycling performance of lithium half-cells. The results showed that, using AMMA binder, both graphite and LiMn_2O_4 could be cycled well in 1 M LiPF_6 3:3:4 (weight) PC/EC/EMC electrolyte with less capacity fading. AMMA is chemically more stable than poly(vinylidene fluoride) (PVDF) against the lithiated graphite. More importantly, AMMA can help graphite to form a stable solid electrolyte interface (SEI) film. An impedance study showed that the SEI film formed with AMMA is more stable than the one formed with PVDF. Therefore, self-delithiation of the lithiated graphite can be reduced by use of AMMA instead of PVDF, which improves the storage performance of Li-ion batteries. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Poly(acrylonitrile-methyl methacrylate); Poly(vinylidene fluoride); Binder; Graphite electrode; Li-ion battery

1. Introduction

In the current Li-ion technology, poly(vinylidene fluoride) (PVDF) has been used as a binder for both the graphite anode and the lithium transitional metal oxide cathode because of its good electrochemical stability and adhesion to the electrode materials and current collector [1,2]. However, it has been found that at elevated temperatures PVDF might react with lithiated graphite (Li_xC_6) and metal lithium to form more stable LiF and unsaturated $>\text{C}=\text{CF}-$ bonds [2–4]. In particular, the reaction of PVDF and metal lithium led to an enthalpy as high as 7180 J/g PVDF [3], while metal lithium was often present within Li-ion batteries when they were over-discharged or charged at low temperatures. Therefore, the reactivity of PVDF with the lithiated graphite and metal lithium has been one of the major concerns for thermal runaway of Li-ion batteries under abuse conditions [2–4]. In addition, PVDF is readily swollen, gelled or dissolved by non-aqueous liquid electrolytes, especially at elevated temperatures, and it is often used as a host polymer for gel polymer electrolyte (GPE) [5–7]. As a result of PVDF swelling or dissolving, adhesion of the electrode materials to the current collector deteriorated, which can cause an increase in the contact resistance between electrode

materials. Therefore, it is desirable to seek an alternative binder that can overcome these drawbacks of PVDF.

Polyacrylonitrile (PAN) has been long adopted as host polymer for GPEs due to its high polarity, good electrochemically stability and solubility in non-aqueous liquid electrolytes [8–11]. In particular, it has been proven that the GPEs made of PAN and LiPF_6 are fire-retardant [10,11], which helps to reduce the abuse hazard of the batteries using them. However, PAN failed to serve as a binder for the electrodes due to its high crystallinity. We found that the electrode films bonded with PAN were too fragile to adhere to the metal substrates (Cu for graphite and Al for cathode). Thus, PAN must be chemically modified so that it can serve as a binder.

Copolymerization has been known to be very effective in improving of the physical properties of polymers. Therefore, we selected poly(acrylonitrile-methyl methacrylate) (AMMA, with AN/MMA = 94:6) copolymer to solve the drawbacks of PAN and PVDF. Previous work showed that substitution of AMMA for PVDF in the graphite electrode might greatly reduce heat release of the lithiated graphite and electrolyte reactions [12]. That is, total enthalpies for the reactions of fully lithiated graphite (MAG-10, Hitachi Chemical) and electrolyte (1.2 M LiPF_6 3:7 EC/EMC) in the temperature range of 280–340 °C were 1211 J/g for AMMA versus 2699 J/g for PVDF. In this work, we evaluated the cycling performance of Li/graphite and Li/ LiMn_2O_4

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half-cells with AMMA binder and 1 m LiPF₆ 3:3:4 PC/EC/EMC electrolyte.

2. Experimental

PVDF (MW = 350,000) and AMMA (MW = 100,000, AN/MMA = 94:6) were purchased from Polysciences, Inc. and used as a binder. Spinel LiMn₂O₄ (SP30, EM Industries, Inc.) and natural graphite (LF-18A, International Technology Exchange Society) were coated onto Al and Cu foil, respectively, by using *N*-methyl pyrrolidinone (NMP) solvent and carbon black conductive agent. The composition of the electrodes was 82% LiMn₂O₄, 10% carbon black, and 8% binder for the cathode, and 95% graphite and 5% binder for the anode. The resulting electrode films were cut into circular disks with an area of 1.27 cm², followed by drying at 120 °C for 16 h under vacuum prior to use.

High purity LiPF₆ (>99.9%, Stella Chemifa Corp.), ethylene carbonate (EC, battery grade, Grant Chemical), and propylene carbonate (PC, battery grade, Grant Chemical) were used as received. Ethyl methyl carbonate (EMC, water content <30 ppm, Mitsubishi Chemical Co.) was dried using activated alumina before use. Electrolyte with a composition of 1 m LiPF₆ 3:3:4 PC/EC/EMC (weight) was prepared and its water content, determined by Karl–Fisher titration, was 10–15 ppm. Using Celgard[®] 2500 membrane as separator, 2325 coin-type Li/LiMn₂O₄ and Li/graphite half-cells were assembled and filled with 150 μl of electrolyte. All operations above were carried out in an argon-filled glove box with both oxygen and water contents of <20 ppm.

An EG&G PAR Potentiostat/Galvanostat Model 273A controlled by a personal computer was used for the measurements of cyclic voltammetry and the scanning rate was 0.01 mV/s. Solartron SI 1287 Electrochemical Interface and SI 1260 Impedance/Gain-Phase Analyzer, driven by Zplot softwares (Scribner and Associates, Inc.), were used for the measurement of electrochemical impedance spectroscopy (EIS) of the cells. The EIS was potentiostatically measured by applying a dc bias potential, whose value equals to open-circuit voltage (OCV) of the cells, and an ac oscillation of 5 mV over the frequency range of 100 kHz to 0.01 Hz. The EIS data were fitted using ZView software (Scribner and Associates, Inc.). Cycling test and OCV recording of the lithium half-cells were performed on a Maccor Series 4000 tester.

3. Results and discussion

3.1. AMMA versus PVDF

In electrodes, the polymeric binder bonds electrode materials together and to the current collector by surrounding the surface of electrode materials and conductive carbon black, if added, to form a continuous film between the particles of

the electrode materials. That is, the electrode materials are directly in contact with the binder molecules. Therefore, the chemical stability of the binder with respect to the electrode materials, especially at fully charged state, is critical to the performance of Li-ion batteries. For the cathode side, both PVDF and AMMA are oxidatively stable at the potentials of the cathode. While for the graphite anode, the merits of the AMMA binder become obvious. During cycling or long-term storage, PVDF reacts not only with metal lithium but also with lithiated graphite. Such reactions are often promoted by an increase of the temperature and are very exothermic. Therefore, the reactivity of PVDF with lithiated graphite and metal lithium has become a safety concern for Li-ion batteries under abuse conditions. On the other hand, the reaction products of PVDF, such as LiF and unsaturated fluoropolymers, may change the composition and morphology of the SEI film and hence affect cell performance. This hypothesis has been confirmed as follows. Cycling performance of the plastic Li-ion batteries using poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) polymer was decreased with an increase of HFP content in copolymer [13] because fluorides in HFP are more active than those in PVDF.

We previously found [14] that PVDF could be dissolved into non-aqueous liquid electrolyte to form a viscous fluid or GPE, depending on the ratio of PVDF and liquid electrolyte. As a result of PVDF dissolution into liquid electrolyte, cell performance deteriorated since the binder failed to bond electrode materials, which led to an increase in the contact resistance between the electrode materials. We also found that AMMA is more difficult to swell or dissolve by non-aqueous liquid electrolyte while it has similar bonding ability as PVDF. Therefore, from the standpoint of chemical stability against lithiated graphite and solubility in liquid electrolyte, AMMA qualifies as a binder for electrodes, especially the graphite anode, of Li-ion batteries.

3.2. Cyclic voltammogram of lithium half-cell

As a binder, AMMA must be electrochemically stable at the potentials at which both anode and cathode operate. Therefore, we first used natural graphite and spinel LiMn₂O₄ to evaluate the electrochemical stability of AMMA. Considering the fact that, in the initial few cycles, electrolyte components (especially solvents) are decomposed on the surface of both graphite [15–17] and LiMn₂O₄ [17–19] to form a so-called solid electrolyte interface (SEI) film, we chose the third cycle to examine the qualifications of AMMA as a binder. The cyclic voltammogram (CV) of graphite and LiMn₂O₄, respectively, with 1 m LiPF₆ 3:3:4 PC/EC/EMC electrolyte is shown in Fig. 1. It is seen that the CV of graphite consists mainly of three pairs of reversible and overlapped current peaks between 0.3 and 0 V, which reflects typically the electrochemical processes for intercalation and deintercalation of lithium ions. According to previous reports [20,21], these current peaks, respectively, reflect such three

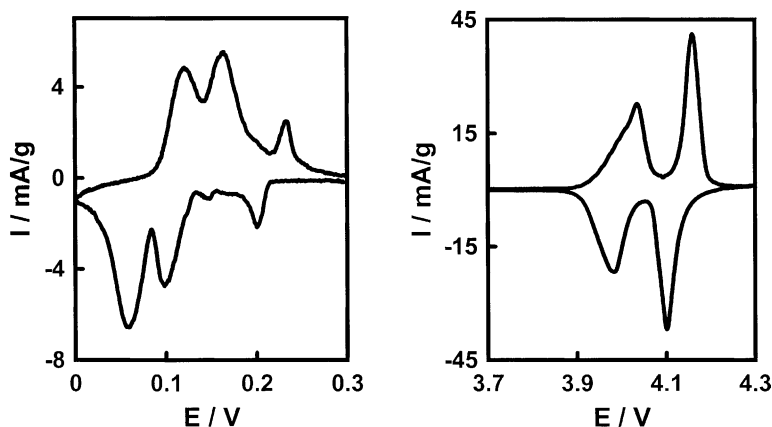


Fig. 1. Cyclic voltammograms of Li/graphite and Li/LiMn₂O₄ half-cells with 1 m LiPF₆ 3:3:4 PC/EC/EMC electrolyte, which were recorded from the third cycle at a scanning rate of 0.01 mV/s.

phase transitions as (i) LiC₇₂ ↔ LiC₃₆, (ii) LiC₂₇ ↔ LiC₁₈ and (iii) LiC₁₂ ↔ LiC₆. The broad plateau currents between the peaks are related to two additional phase transitions, which have not been identified [21]. On the other hand, the CV of LiMn₂O₄ is composed of two pairs of reversible and well-separated current peaks in the voltage range of 3.8–4.2 V. These current peaks are known to reflect these two reversible phase transitions of LiMn₂O₄ ↔ Li_{0.5}Mn₂O₄ ↔ λ-MnO₂ [22,23].

In Li-ion chemistry, the potential of the graphite anode is generally limited by the electrochemical deposit ion of metal lithium around 0 V versus Li⁺/Li. As Fig. 1 shows, there is no additional reductive current following the end of intercalation of lithium ions into graphite. On the contrary, the

potential of LiMn₂O₄ cathode may be higher than that of λ-MnO₂ (at fully charged state) in the case of overcharge. Therefore, the binder must stand higher oxidation potentials. It is observed from Fig. 1 that the oxidative current fell to zero after LiMn₂O₄ was completely delithiated, showing that AMMA is oxidatively stable. The results described above show that AMMA is electrochemically stable with respect to both graphite and LiMn₂O₄, and that it is qualified as a binder for the electrodes of Li-ion batteries.

3.3. Cycling performance of lithium half-cells

Fig. 2 plots voltage–capacity curves of the first cycle for Li/graphite and Li/LiMn₂O₄ half-cells with 1 m LiPF₆ 3:3:4

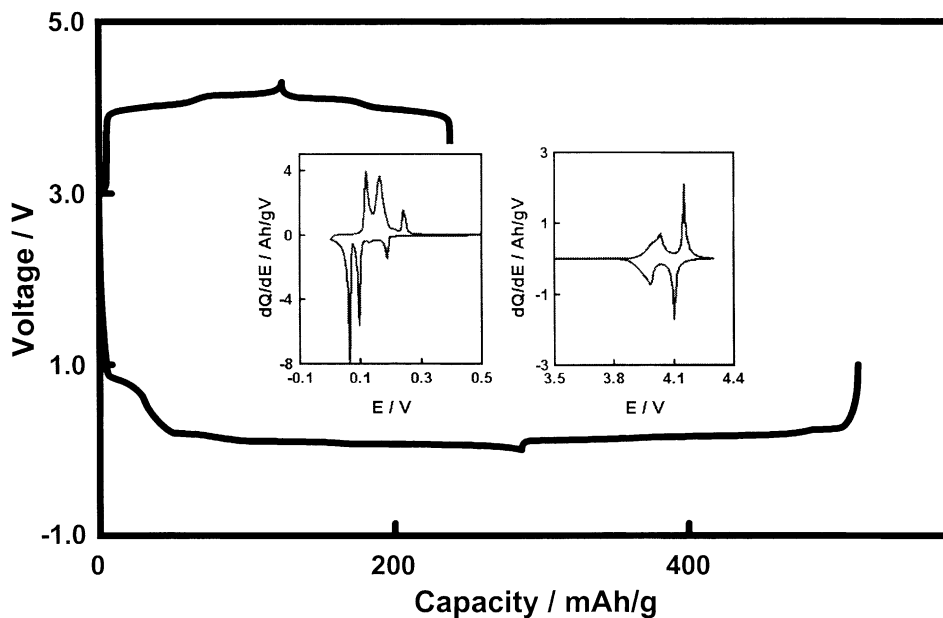


Fig. 2. Voltage–capacity curves of Li/graphite and Li/LiMn₂O₄ half-cells with 1 m LiPF₆ 3:3:4 PC/EC/EMC electrolyte, which were recorded from the first cycle at 0.1 mA/cm². Inset shows the correlation between differential capacity and cell voltage of the half-cells.

PC/EC/EMC electrolyte, in which AMMA was used as a binder for both graphite and LiMn_2O_4 electrodes. It can be observed that both cells showed a small amount of irreversible capacity in the initial periods. This irreversible capacity is known to originate from the decomposition of electrolyte solvents, which leads to the formation of the SEI film on the surface of both electrodes [15–19]. It is evaluated from Fig. 2 that the capacity and cycling efficiency of LiMn_2O_4 are 114 mA h/g and about 90%, respectively, and those of graphite are 228 mA h/g and 79%, respectively. These values are comparable with our early results that were obtained from PVDF binder and 1 m LiPF_6 3:7 EC/EMC electrolyte [17]. Inset in Fig. 2 shows the differential capacities of graphite and LiMn_2O_4 versus cell voltage, which are selected from the reversible voltage regions. Consistency between differential capacity plots (inset in Fig. 2) of the first cycle and CVs (Fig. 1) of the third cycle shows that AMMA binder is stable during the initial formation of graphite anode and LiMn_2O_4 .

The capacities of Li/graphite and Li/ LiMn_2O_4 half-cells using AMMA binder are plotted in Fig. 3 as a function of the cycle number. It can be seen that, after a slight increase in the initial few cycles, the capacity of the Li/graphite cell remained invariant with cycle number. The stable capacity of graphite was around 210 mA h/g, which was lower than the theoretical value (372 mA h/g). Thus, the initial increase of the capacity may be ascribed to an increase in the utilization of graphite active materials. For Li/ LiMn_2O_4 cell, capacity of LiMn_2O_4 started with 110 mA h/g, followed by a slow capacity fading. After 200 cycles, the capacity of LiMn_2O_4 fell to 100 mA h/g, which corresponds to a fading rate of 0.045% per cycle. Capacity fading of LiMn_2O_4 has been well understood, which may involve (i) structure-related Jahn–Teller distortion [24], (ii) chemical dissolution of electrode active materials (Mn^{3+}) [25,26] and (iii) structural degradation [27]. Therefore, the observed capacity fading (Fig. 3) may arise from LiMn_2O_4 instead of AMMA and electrolyte.

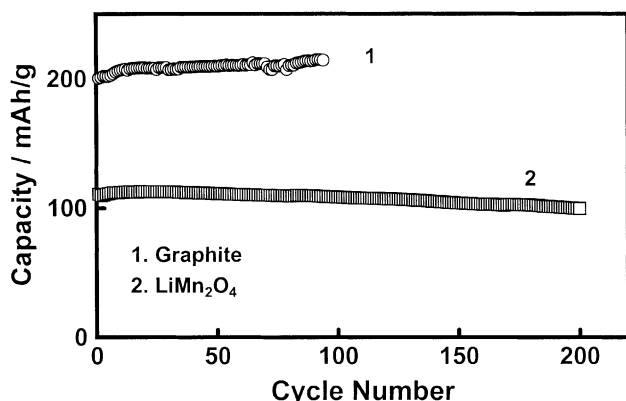


Fig. 3. Cycling performance of lithium half-cells with 1 m LiPF_6 3:3:4 PC/EC/EMC electrolyte, which was obtained by cycling the cells at 0.3 mA/cm² between 0.002 and 1.0 V for Li/graphite cell, and at 0.5 mA/cm² between 3.3 and 4.3 V for Li/ LiMn_2O_4 .

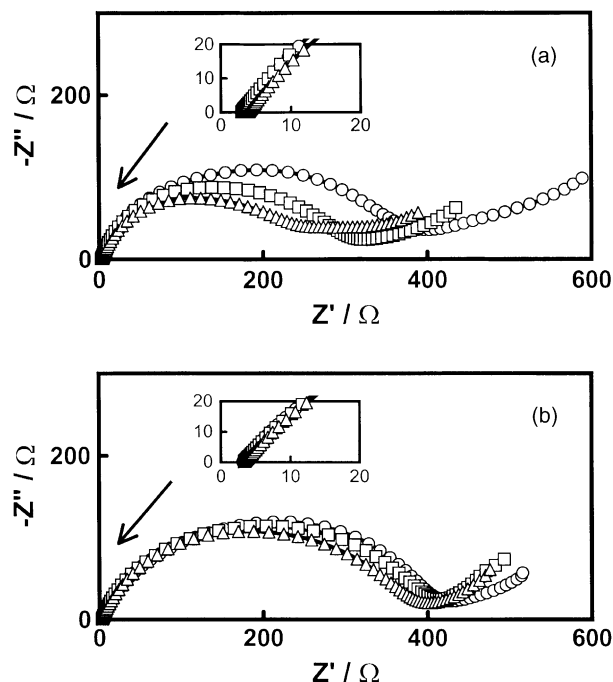


Fig. 4. Nyquist plots of the fully lithiated Li/graphite half-cells using different binder after storage at 60 °C for 0 day (circle), 2 days (square), and 7 days (triangle). (a) PVDF and (b) AMMA.

3.4. Stability of SEI film on graphite

To examine the suitability of the AMMA binder for the graphite anode of Li-ion batteries, we studied the stability of SEI film on the graphite surface. For the purpose of comparison, impedance spectra of two graphite electrodes employing PVDF and AMMA, respectively, were measured. Nyquist plots of the fully lithiated Li/graphite half-cells with different storage times at 60 °C are shown in Fig. 4. In general, the impedance spectra of Li/graphite cells are composed of two partially overlapped semicircles at high and medium frequencies and a straight sloping line at low frequencies [28,29]. The semicircle at high frequencies reflects SEI resistance (R_f) and the one at low frequencies reflects charge-transfer resistance (R_{ct}), while the intercept of the spectrum and image impedance axis at the far high frequency end corresponds to electrode and electrolyte bulk resistance (R_e).

It is evaluated from Fig. 4 that the R_e of both cells using PVDF and AMMA, respectively, is about 3 Ω and it is independent of the binder and the storage time. This result reveals that the binder has negligible impact on the conductivity of graphite electrodes. However, the R_f , fitted by ZView software, exhibits an important difference between PVDF and AMMA. With an increase of the storage time, the cell using PVDF shows a decreased R_f , while that using AMMA is nearly invariant. It is considered that the decreased R_f during the storage at elevated temperatures is linked to the dissolution of SEI film. More stable impedance spectra (Fig. 4b) against the storage time suggest that

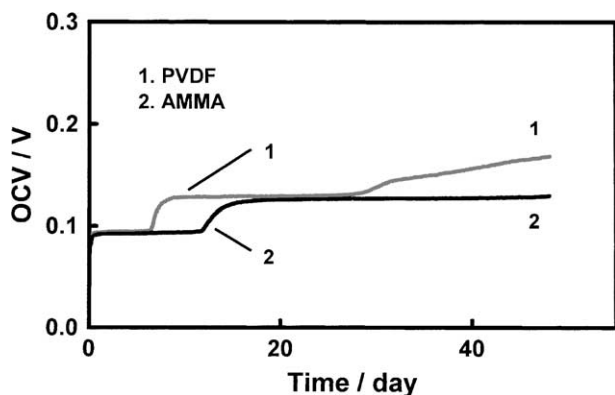


Fig. 5. Increase of OCV with the storage time at 60 °C for the fully lithiated Li/graphite half-cells using different binders.

AMMA would be a better binder for the graphite anode of Li-ion batteries, as compared to PVDF.

3.5. Self-delithiation of the lithiated graphite

Fig. 5 compares the change of open-circuit voltage (OCV) with the storage time at 60 °C for two fully lithiated Li/graphite half-cells using PVDF and AMMA, respectively. After recovery from the polarization during the previous lithiation, both cells showed an identical the OCV (0.09 V), which reflects the potential of a fully lithiated graphite versus Li⁺/Li. With an increase of the storage time, the OCV was increased. This behavior is very similar to that of the voltage–capacity plot in the charging process (delithiation) of Li/graphite cell (Fig. 2). If the IR drop caused by galvanostatic delithiation in Fig. 2 is deducted, the plateau voltages in Figs. 2 and 5 are in very good agreement. Therefore, the spontaneous increase in the OCV, as shown in Fig. 5, can be ascribed to self-delithiation of the lithiated graphite, which corresponds to a self-discharge process in the Li-ion batteries. The mechanism of the self-delithiation may be a local reduction–oxidation process, which is associated with the solvent reduction and graphite delithiation. The capacity loss resulting from self-delithiation can be recovered in the following lithiation.

Consistent with normal delithiation, the OCV of Li/graphite cells increases with the storage time through three distinct plateaus. It can be seen from Fig. 5 that, at 60 °C, the OCV of Li/graphite cell using PVDF passed through two plateaus in 30 days and kept continuously increasing, while the cell with AMMA, remained on the second plateau after 50 days of the experiment. These results reveal that AMMA can help the lithiated graphite to reduce self-delithiation, and hence increase the calendar life of Li-ion batteries.

4. Conclusions

It may be concluded that poly(acrylonitrile-methyl methacrylate) (AMMA, with AN/MMA = 94:6) is suitable

as the binder for both graphite anodes and lithium transitional metal oxide cathodes of Li-ion batteries. For graphite anodes, in particular, AMMA is better than PVDF that has been widely used in the current Li-ion technology. AMMA binder can help graphite to form more stable SEI films. Use of AMMA binder favors reduced self-delithiation of the lithiated graphite, and therefore increases the calendar life of Li-ion batteries.

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