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Short communication

Poly(acrylonitrile-methyl methacrylate) as a non-fluorinated binder for the graphite anode of Li-ion batteries

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1. Introduction

Poly(vinylidene fluoride) (PVDF) has been a choice of the binder for both cathode and graphite anode in state-of-the-art Li-ion batteries [1, 2]. However, there is currently a demand to replace PVDF with non-fluorinated binder since at elevated temperatures the fluorinated polymers react with lithiated graphite (Li_xC_6) and metal lithium to form more stable LiF and $>C{=}CF-$ double bonds. In particular, the reaction of PVDF and metal lithium produces an enthalpy as high as 7180 J $(g\ PVDF)^{-1}$ [1]. It has been reported that in the presence of electrolytes, PVDF and lithiated graphite undergo a series of exothermic reactions, including (i) temperature-induced degradation of the solid electrolyte interface (SEI) at 120–140 °C, (ii) reactions of lithiated graphite and electrolyte at 210–230 °C, and (iii) dehydrofluorination of PVDF initiated by Li_xC_6 at >260 °C [1, 2]. Among these reactions, the last one is known to be very exothermic and is believed to be a potential source for the thermal runaway of Li-ion batteries under abuse conditions. Therefore, safety concerns with Li-ion batteries may arise from the use of PVDF in the graphite anode.

To replace the rather reactive PVDF, we attempt to evaluate poly(acrylonitrile-methyl methacrylate) (AMMA) as a non-fluorinated binder for the graphite anode of Li-ion batteries. Differential scanning calorimetry (DSC) study has shown that the heat of reaction of the lithiated graphite and electrolyte can be reduced significantly by using AMMA instead of PVDF [3]. That is, total enthalpies for the reactions (as indicated by two exothermic peaks in DSC curves) of the fully lithiated graphite (MAG-10, Hitachi Chemical) and electrolyte (1.2 M $LiPF_6$ 3:7 EC/EMC) in the temperature range 280–340 °C can be reduced to 1211 J $(g\ AMMA)^{-1}$ from 2699 J $(g\ PVDF)^{-1}$. In this paper, we will electrochemically evaluate AMMA as a binder of the graphite anode of Li-ion batteries.

2. Experimental details

$LiPF_6$ (>99.9%, Stella Chemifa Corp.), ethylene carbonate (EC, battery grade, Grant Chemical), and propylene carbonate (PC, battery grade, Grant Chemical) were used as received. Ethylmethyl carbonate (EMC, water content <30 ppm, Mitsubishi Chemical Co.) was dried using activated aluminum oxide before use. Natural graphite (distributed by International Technology Exchange Society, code LF-18A) was coated onto Cu foil with 5 wt % of either PVDF (MW = 350 000, Polysciences, Inc.) or AMMA (MW = 100 000, AN/MMA = 94:6, Polysciences, Inc.) binder by using *N*-methyl pyrrolidinone (NMP) solvent.

In an argon-filled glove box with both water and oxygen contents less than 20 ppm, an electrolyte was prepared by dissolving 1.0 m (mole solute per kilogram solvent) $LiPF_6$ in a 3:3:4 (wt) PC/EC/EMC mixed solvent. The water content of the resulting electrolyte, as determined by Karl-Fisher titration, was 10–15 ppm. In the same glove box, BR2335-type Li/graphite button cells with an electrode area of 1.27 cm^2 were assembled and filled with 150 μL of liquid electrolyte. A Maccor Series 4000 tester was used to perform galvanostatic cycling test and to record the open-circuit voltage (OCV) of the cells. A constant temperature environment for calendar life testing of the fully lithiated (discharged) Li/graphite cells was provided by a Tenney Environmental Oven Series 942.

3. Results and discussion

3.1. *AMMA vs PVDF*

To qualify AMMA as a binder for the graphite anode, the bonding ability of AMMA was first examined by comparing it with PVDF. In this experiment, 5 wt % of

AMMA and PVDF, respectively, was used to coat graphite with the same loading onto Cu foil. The resulting films were dried at 120 °C under vacuum for 6 h, and then subjected to a 'scratch off' testing by using a knife to scratch the graphite coating off the Cu foil. This testing showed that AMMA has very similar bonding ability as PVDF. The same result was also obtained from a 'peel-off' test by sticking 3 M Scotch type on the graphite coating and then peeling it off the coating. The above two experiments indicate that from the point view of bonding ability, AMMA is suitable for a binder. It should be mentioned that 6% of MMA component in the AMMA copolymer plays a very important role in improving the bonding ability of AMMA. We have examined poly(acrylonitrile) homopolymer, which is the main component of the AMMA copolymer, as a binder, and found that it is unable to bond graphite onto Cu substrate. The graphite films bonded with poly(acrylonitrile) are too fragile to be handled in the cell assembly.

Low solubility of the binder in liquid electrolytes is essential for the electrode film to retain its mechanical stability in the course of battery operation and storage. Therefore, we compared the solubility of PVDF and AMMA in a 1.0 m $LiBF_4$ 1:1 (wt) PC/EC electrolyte. In this experiment, we heated an 85:15 (wt) mixture of the liquid electrolyte and binder in a sealed glass vial at 130 °C. After 0.5 h, we found that PVDF had been dissolved to form a viscous fluid, while AMMA still remained in a transparent rubber state. Upon cooling, both mixtures became a transparent polymer gel electrolyte with a significant difference in the mechanical strength. This experiment indicates that AMMA is less soluble in the liquid electrolyte, as compared to the PVDF that has been most widely used in state-of-the-art Li-ion batteries. It is because of its high solubility in the liquid electrolytes that PVDF has been used to make polymer gel electrolytes by many researchers [4–7].

3.2. *Galvanostatic cycling*

In the graphite anode of Li-ion batteries, the binder molecules surround graphite and additives (highly conductive carbons, if used) to form a continuous film and bond the film to Cu substrate. Therefore, the properties of the binder may greatly affect the formation of SEI film on the graphite surface, which is usually completed in the initial few lithiation and delithiation cycles. Figure 1(a) and (b) show voltage–capacity curves and differential capacity–voltage plots for the initial three cycles of the graphite electrodes using PVDF and AMMA, respectively. The coulombic efficiency (CE) of the first cycle is relatively low (~70%), however, it gradually increases up to 100% with progressive cycling. It is calculated that CEs of the initial three cycles of the graphite electrode with PVDF are, respectively, 68.6%, 92.6%, and 94.4% (Figure 1(a)), while those with AMMA are, respectively, 70.0%, 93.1%, and 96.1% (Figure 1(b)). Although the CE difference caused by these two binders is small, the results are very reproducible. We have used other carbons to repeat the above experiment and obtained very similar results. It should be noted that the current density greatly affects the CE of the forming cycles since the newly formed SEI film on the graphite surface undergoes these two reverse processes of (i) progressive growth and (ii) dissolution back to the electrolyte solution. Slow forming (i.e., low current density) allows longer time for the dissolution of the SEI film, which consequently results in a lower CE. Therefore, more cycle numbers are needed to complete the formation of SEI film when a low current density is employed. In the present work, the measured CEs are rather low since we used a very low current density (0.03 mA cm^{-2}).

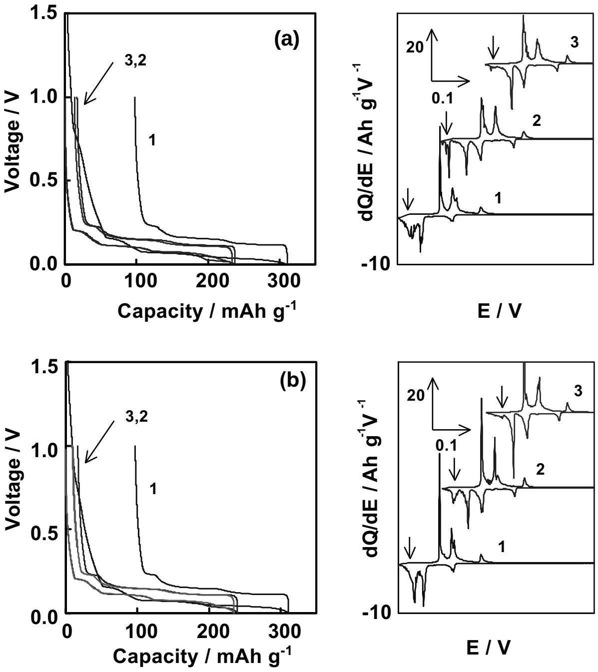

Fig. 1. Voltage–capacity curves and differential capacity–voltage plots of graphite electrodes with different binders recorded at 0.03 mA cm^{-2} from the initial three cycles. For clarity a shift has been added to the differential capacity–voltage plots of the 2nd and 3rd cycles. (a) PVDF and (b) AMMA. Current efficiency, for (a): (1) 68.6%, (2) 92.6% and (3) 94.4%; for (b): (1) 70.0%, (2) 93.1% and (3) 96.1%.

In previous work [8], we found that during the initial forming cycles the highly conductive SEI film on the graphite surface is mainly formed in the voltage range 0.25–0.04 V. Therefore, we are interested in examining the effect of binders on the initial irreversible capacity of the graphite electrodes in this voltage range. As shown by the differential capacity–voltage plots in Figure 1(a) and (b), the first reduction (lithiation capacity) peak, which normally appears at ~0.2 V and corresponds to the transition of $LiC_{72} \leftrightarrow LiC_{36}$, shifted to lower potentials (at ~0.15 V, see curve 1) in the first lithiation process and returned to its normal position in the subsequent cycles (see curves 2 and 3). It is interesting to note that the irreversible reduction peaks below 0.06 V,

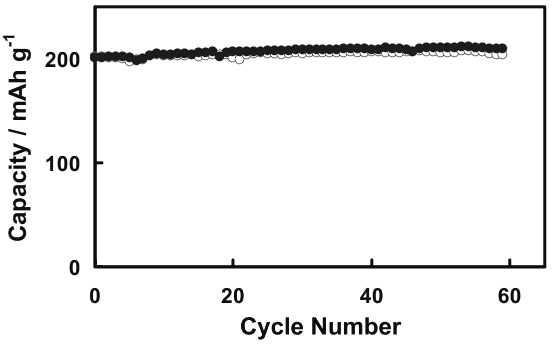

Fig. 2. Delithiation capacities of graphite electrodes with different binders as a function of the cycle number measured by galvanostatically cycling Li/graphite cells at 0.5 mA cm^{-2} between 0.002 and 1.0 V. Key: (○) PVDF, (●) AMMA.

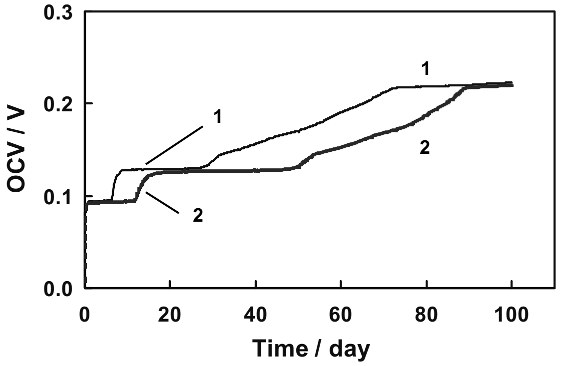

Fig. 3. Effect of binders on OCV stability of fully lithiated Li/graphite cells at 60 °C. Key: (1) PVDF and (2) AMMA.

as indicated by arrows in Figure 1, gradually decrease with cycle number and nearly vanish in the third cycle at which the CE has approached 100%. It is obvious that the difference in the CEs between PVDF and AMMA resulted from the irreversible reductions that take place below 0.06 V.

Delithiation (charge) capacities of two Li/graphite cells using PVDF and AMMA, respectively, are plotted as a function of cycle number in Figure 2, which shows that the cells have nearly the same cycling performance. This observation shows that the AMMA binder has no adverse impact on the cycling performance of the graphite electrode. Therefore, we may conclude that AMMA is electrochemically stable as a binder of the graphite anode in Li-ion batteries.

3.3. *Storage performance*

The chemical stability of the AMMA binder against the lithiated graphite can be evaluated by observing the OCV change of a fully lithiated Li/graphite cell. Figure 3 shows the OCV change of two fully lithiated Li/graphite cells using PVDF and AMMA, respectively, with storage time at 60 °C. The OCV slowly rises with storage time through three voltage plateaux. This behaviour is very similar to the voltage–capacity curve of a normal delithiation (charge) process of the Li/graphite cells (see Figure 1). If considering the IR drop caused in a practical charge process of the Li/graphite cells, it is seen that the voltage regions of each plateau in Figure 1 and 3 are consistent with each other. Furthermore, the capacity loss of the above cells in storage can be recovered in the subsequent lithiation. Therefore, we consider that the observed OCV increase in Figure 3 is a simple self-delithiation process, which can be described by the reaction:

$$\mathrm{Li}_x\mathrm{C}_6 \rightarrow \mathrm{Li}_{x-\delta}\mathrm{C}_6 + \delta\mathrm{Li}^+ + \delta\mathrm{e}^-$$

Such a self-delithiation can be ascribed to a local redox process [9]. That is, these two reverse processes of graphite delithiation (oxidization) and electrolyte reduction must simultaneously take place in the vicinity of the graphite electrode. It is known that the solvent reduction is closely associated with the stability of SEI film. Therefore, we may use OCV change to evaluate the stability of the SEI films formed with the different binders. Figure 3 indicates that during storage at 60 °C, the OCV of the cell using AMMA binder increases more slowly. This implies that the SEI film formed with the AMMA binder is more stable. Therefore, we conclude that from the standpoint of SEI stability, AMMA is better than PVDF as a binder for the graphite anode of Li-ion batteries.

4. Conclusions

Poly(acrylonitrile-methyl methacrylate) (AMMA) is a good binder for the graphite anode of Li-ion batteries. With an advantage of substantially lower solubility in the liquid electrolytes, AMMA has a similar bonding ability as poly(vinylidene fluoride) binder. AMMA can well withstand the attack of the highly reactive lithiated graphite. Furthermore, the presence of AMMA facilitates the formation of a stable solid electrolyte interface.

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