

The Effect of Nano-sized SEI Film Formed by Vinyl Acetate Additive for Li-ion Batteries

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The electrochemical performance of Li/graphite and LiCoO₂/graphite cells were investigated in 1 M LiPF₆ dissolved in propylene carbonate (PC) + dimethyl carbonate (DMC) (Vol. 1:2) alone and with 1 wt.% vinyl acetate (VA) additive in this study. Decomposition of solvents at graphite electrode could be remarkably suppressed by addition of the VA additive in the electrolyte, leading to the improvement of electrochemical performances of the cells. We found that the VA additive should give a solid electrolyte interphase (SEI) on the surface of graphite electrode, which effectively suppressed the PC decomposition in the electrolyte.

Since 1990, Sony announced the commercial availability of "lithium ion rechargeable battery" based on a carbon and a LiCoO₂ cathode material, extensive researches continued to obtain the better battery performances. Although it was mainly focused in electrode materials and electrochemical characteristics in the basic research, additives also have been received the intense attention in practical application of lithium secondary batteries. Especially, it is well known that graphite in the propylene carbonate (PC)-based electrolytes showed a serious problem; it is unstable when lithium is intercalated and co-intercalation with solvent molecules induces the exfoliation of the graphite into the electrolyte. Therefore, many research trials were conducted to form a high quality of solid electrolyte interphase (SEI) onto the various electrodes. The well-formed SEI layer by adding various additives could suppress the decomposition of electrolyte solvents, which prohibited the leakage of electrolyte and improved the cycling performance of lithium ion batteries.¹⁻⁶

We have reported a new concept that catechol carbonate and its derivatives could be good candidates as additives and the addition of them into the electrolyte remarkably improved battery performance.^{1,2} We also proposed the mechanism of the formation for SEI film and the suppression of PC decomposition on the graphite anode in 1 M LiPF₆/PC-DEC (1:1 in vol.) with a 1,3-benzodioxol-2-one electrolyte system.¹

According to a series of recent experiments, we can know the unique effects of some additives into the PC-based electrolytes, such as divinyl adipate (ADV), allyl methyl carbonate (AMC), ethylene sulfite (ES), and vinyl acetate (VA), which could be good candidates of additives for lithium ion battery. In order to choose a good additive, many physicochemical properties were considered including the stability in the electrolyte, the degree of decomposition prior to solvents to form stable SEI films on anodes, and the thickness and contents of SEI layer when used for practical cell. We report in this study, one of these additives, vinyl acetate exhibited the most effective to improve the cycling performance for lithium ion batteries.

Vinyl acetate was commercially available from Aldrich and used without further purification. LiPF₆ was battery grade as received from UBE industries. Propylene carbonate, ethylene

carbonate, dimethyl carbonate, and methyl ethyl carbonate were stored under a nitrogen atmosphere.

A three-electrode glass cell was used for cyclic voltammetry (CV) measurement. The working electrode was consisted of 3 mg of the graphite and 2.2 mg of conducting binder (TAB), which pressed onto stainless steel mesh. The counter and reference electrodes were prepared by pressing lithium foil onto stainless steel gauze. The used electrolyte was 1 M LiPF₆ + PC/DMC (1:2 in vol.) alone or with 1 wt.% VA additive. The CV measurement was performed with an Arbin Instruments Model MSTAT4 battery test system at 0.2 mV/s scan rate between the voltage limits of 0.0–2.0 V. All assembling of the cells were carried out in a dry box with argon gas. The particle size and morphology of the graphites were observed using a scanning electron microscope (SEM, JSM-5300E, Japan). The binding energies of LUMOs and HOMOs for solvents and additives were calculated using WinMOPAC 2.0 software. Molecular orbitals were constructed using a molecular orbital theory called Modified Neglect of Diatomic Overlap Parametric Method 3 (MINDO-PM 3).

The electrochemical characterizations were performed using CR2032 coin-type cell. In order to prepare graphite electrode, 90 wt.% of graphite (MCMB 6-28) suspended in a solution of 10 wt.% of poly(vinylidene fluoride) (PVDF) in 1-methyl-2-pyrrolidone was spread on the copper steel current collector and dried at 100 °C for 12 h. It was pressed at 100 kg/cm² and then finally dried under vacuum at 130 °C for 3 h. The cell assembling method and procedure of Li/graphite or LiCoO₂/graphite cells have been described elsewhere.^{1,2} The charge/discharge process were performed at a current density of 0.4 mA/cm² with a cut-off voltage of 2.7–4.2 V at room temperature.

Figure 1(a) shows the charge/discharge curves of the Li/graphite (MCMB 6-28) cells in the PC-based electrolyte alone and with the addition of 1 wt.% VA. For the cell without an additive, only a long discharge plateau is observed, due to the decomposition of PC at around 0.7–0.8 V (no lithium intercalation process). This cell also is impossible to be charged (no lithium de-intercalation process), which suggested that decomposition of PC prevented the formation of an effective surface layer on graphite surface. This consequently results in the exfoliation of the graphite electrode. On the other hand, in case of the addition 1 wt.% VA (Figure 1(b)), there is no long discharge plateau and no obvious plateau at around 0.7 V in the discharge curve. Moreover, the CV profile clearly shows the effect of VA additive, which suppress the decomposition of PC. In case of no additive into the electrolyte, although it was not shown here, the decomposition of PC began at about 0.82 V and the cathodic current became more larger in the lower potential direction, and eventually, no anodic peak due to delithiation was observed during reverse scanning. However, when added 1 wt.% VA additive (Figure 1(c)) shows that very small cathodic current starts to appear at potentials higher than 0.82 V together with a small cathodic peak at about 0.5 V. Additionally, completely reversible

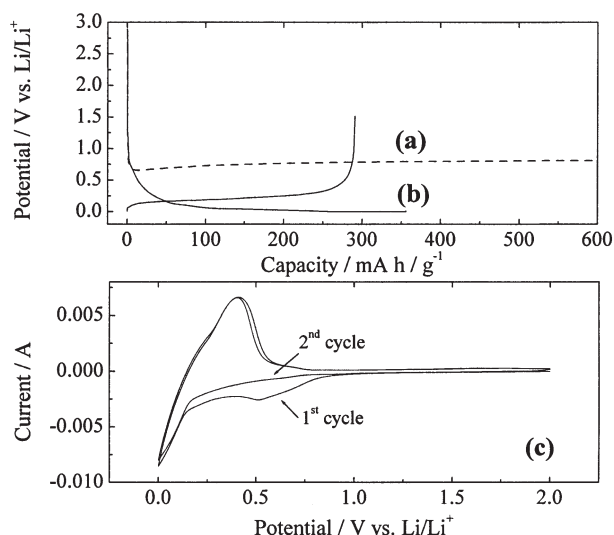


Figure 1. Charge/discharge profiles of Li/natural graphite cell (a) without additive, (b) with 1 wt.% VA additive, and (c) cyclic voltamogram of (b).

intercalation/de-intercalation of lithium into/from graphite reaches at the second cycle. We suggest that the reduction current above 0.5 V during the first cathodic scanning be mainly blamed for the decomposition of VA, otherwise, the graphite electrode would be damaged by the decomposition of PC. The improvement of electrochemical performance of graphite electrode was benefited from high quality decomposition product of VA. These results clearly showed that the added VA additive could be formed an effective surface layer to suppress the decomposition of PC.

The morphologies of the both Li/graphite electrodes after 3th cycle, without and with addition of 1 wt.% VA additive, were observed using a scanning electron microscope (SEM). Figure 2(a) shows that the graphite without additive made a large amount of exfoliation, due to the massive co-intercalation with solvent and decomposition of PC. It mainly resulted in the graphite electrode destruction. However, the surface of graphite electrode with addition of 1 wt.% VA is well covered with passivated layer without any exfoliation and this layer is composed of small nanoparticle sizes about 50–100 nm as shown in Figure 2(b).

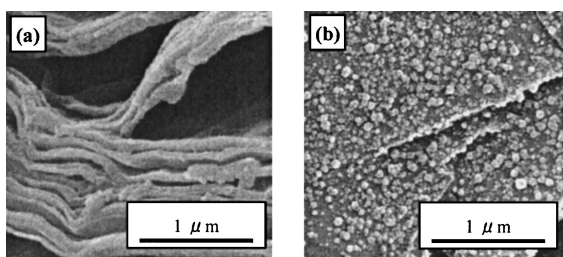


Figure 2. SEM images of Li/graphite cell after 3th cycle (a) without additive, (b) addition of 1 wt.% VA.

In order to investigate the role of VA additive for lithium ion batteries practically, we conducted the cycling test of LiCoO₂/graphite cells with and without VA additive. The cycle performances of the two cells with and without the addition of 1 wt.% VA in the 1 M LiPF₆/PC-DMC (Vol. 1:2) electrolyte. The cell without additive could not be cycled, owing to the reason as described before and its higher crystallinity of graphite. However, the cell with VA

additive showed an excellent cycleability until 50 cycles. The initial discharge capacity was 128 mAh/g and the last one was 108 mAh/g. The cycle retention rate after 50 cycles was 87%. This means that the SEI film, which was formed by the addition 1 wt.% VA, enhanced lithium ion mobility on/into the graphite and could be an important key technique to control cycling performance of lithium-ion batteries.

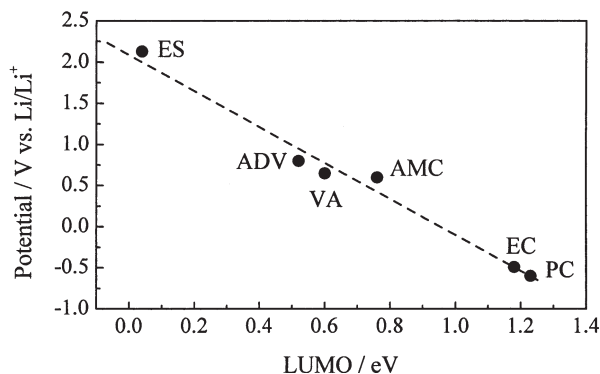


Figure 3. Correlation between LUMOs and reduction potentials for additives and solvents measured at Pt electrode in 1 M LiPF₆/PC-DMC (Vol. 1:2) electrolyte.

Additionally, we found an interesting indication that the VA and other additives (ADV, AMC, and ES) have been reduced prior to PC and DMC to form effective SEI on graphite electrodes. We observed that the reduction order of additives and solvents could be correlated well with their relative values of the lowest unoccupied molecule orbitals (LUMOs). Figure 3 showed a correlation between LUMOs and reduction potentials of the all additives, which were investigated during this study. There are also indicated the characteristics of PC and EC in the same figure. A roughly linear relation between them was clearly observed. It means that additives can be reduced at a higher potential than that of any solvent in the electrolyte, its decomposition product might form a SEI layer to suppress the decomposition of solvents. We also emphasize here that the reduction or oxidation potential of an organic compound was much more complicated than a simple reversible redox reaction. For a simple reversible redox reaction, the reduction potential in solution includes the sum of the electron affinity (E_A) and the change of solvation energy (ΔE_{sol}), while the oxidation potential is the sum of ionization potential (E_I) and the change of solvation energy (ΔE_{sol}) in the case of thermodynamically based equilibrium potentials. For the reduction or oxidation potential of an organic compound, other factors, i.e. bond cleavage and irreversible charge transfer processes involving two or multi-electrons, should be considered. Therefore, we use LUMO and HOMO as only a semi-empirical method for screening possible additives.

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