Suppression of Electrochemical Decomposition of Electrolyte in Lithium Ion Batteries: An Electrolyte Containing Acetate Group

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A group of acetate compounds has been studied as electrolyte additive for lithium ion batteries in order to suppress the electrolyte decomposition on graphite electrode. The amount of 1 wt % additives (acetic anhydride, 1-acetoxy-2-methoxyethane, isopropenyl acetate, and phenyl acetate) facilitates the electrochemical performance of the cell by the suppression of the decomposition of electrolyte. Molecular orbital calculation is used as screening tool for the selection of additives.

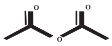
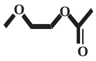
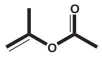
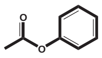
Since commercialization of lithium ion battery, the capacity of lithium ion battery has been greatly increased. The main reason of this increase is applying high crystallinity graphite as an anode material. However, the main drawback of applying graphite is generation of gas produced by decomposition of electrolyte by side reaction of electrode and electrolyte during charge. In order to suppress the decomposition of electrolyte, the technique forming SEI film on the surface of electrode were reported[1–6] and we also have reported surface coating of graphite by carbon.[7,8] The researches were quite effective to increase battery performance. From new concept as mentioned before, we reported catechol carbonate.[1,2] After that, we also reported vinyl compounds[3–5] and succinimide[6] additives, the derivatives can be candidates of additives for anode material. In this research, we have studied electrochemical performance shown by the acetate group compounds in order to investigate the promising role played by additive vinyl acetate (VA).

1 M $LiPF_6$/PC-DMC (dimethyl carbonate) (1:2 v/v) with 1 wt % additives and neat were used. The acetate group compounds were commercially available from Wako Chemical. The carbon electrodes were prepared by spreading a mixture of 90 wt % mesocarbon microbeads (MCMB6-28), 10 wt % polyvinylidene fluoride (PVDF) and 1-methyl-2-pyrrolidone onto a copper foil current collector and dried at 150 °C. The electrodes were pressed at 2 ton cm^{-2}, and finally dried under vacuum at 120 °C for 4 h.

The construction of molecular orbital was performed applying modified neglect a diatomic overlap parametric method 3 (MINDO-PM3) based on molecular orbital theory. The lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) for solvents and additives were calculated using WinMOPAC 2.0 version software. Electrochemical experiments were carried out in three-electrodes glass cell with MCMB6-28 as working electrode, lithium foil as counter and reference electrodes at 1 mV s^{-1} scan rate between the voltages limit 0–2.0 V using HSV-100 (Hokuto Denko). The cycling test was conducted at current of 0.4 mA cm^{-2} with the cut off voltage of 1.5–0.001 V. All assembling of the cells were carried out in an argon filled glove box. The ac impedance was measured using frequency response analyzer (Solartron SI 1250) and potentiostat (Solartron 1287). The X-ray photoelectron spectroscopy (XPS) measurement were performed with a PHI-5800 electron spectroscopy. The sample consisting MCMB6-28 as anode and lithium as cathode were analyzed after the first charge/discharge cycle conducted at current of 0.4 mA cm^{-2} with the cut off voltage of 1.5–0.001 V in 1 M $LiPF_6$/EC-DMC (1:2 v/v) electrolyte with 1 wt % additive. The samples after removing from the cell were washed with DMC and dried in vacuum at room temperature.

Table 1 shows the acetate group compounds with their structure and calculated LUMO and HOMO energies. We have selected additives having low LUMO energy than the electrolyte solvents PC, EC, and DMC (1.235, 1.175, and 1.054 eV, respectively) on the assumption that the additives with low LUMO energy than the solvent reduce at higher potential and in turn suppress the electrolyte decomposition by the efficient film formation.

Table 1. Structures and calculated HOMOs[a] and LUMOs[a] of additives

Additives	Structure	HOMO/eV	LUMO/eV
Acetic anhydride (AA)		−11.4355	0.3847
1-Acetoxy-2-methoxyethane (AME)		−11.1001	0.9827
Isopropenyl acetate (IPA)		−9.8731	0.6635
Phenyl acetate (PA)		−9.3447	0.1821

[a]Standard (i.e., 0 eV): Two atoms at infinity distance in a vacuum.

The charge/discharge profile of a MCMB electrode in 1 M $LiPF_6$/PC-DMC (1:2 v/v) electrolyte alone and with 1 wt % different additives is shown in Figure 1. A long discharge plateau in Figure 1a dashed line at around 0.7 to 0.8 V reveals the exfoliation of the electrode due to decomposition of PC-DMC electrolyte without additive. On the other hand, with the addition of the additives the long plateau has been disappeared as shown in Figure 1 (a, b, c, and d solid line) by suppressing electrolyte decomposition and in turn the intercalation and deintercalation process is facilitated. Out of the twenty acetate compounds only four compounds having an electronegative functional group, i.e., the acetate group directly attached to the carbon–carbon double bond with no steric hindrance (IPA and PA) and additives having more electronegative atoms, i.e., oxygen with no steric hindrance (AA and AME) could suppress the decomposition of the electrolyte. The additives PA and IPA have flat plateaus with irreversible capacity of 176 mA h g^{-1} and 146 mA h g^{-1}, respec-

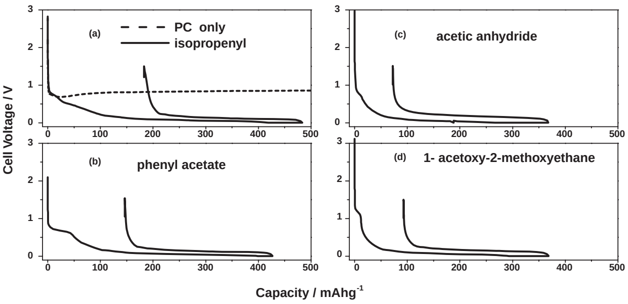


Figure 1. Charge/discharge profile of Li/MCMB6-28 in 1 M $LiPF_6$/PC-DMC (1:2 v/v): without additive, dashed line; with additive, solid line.

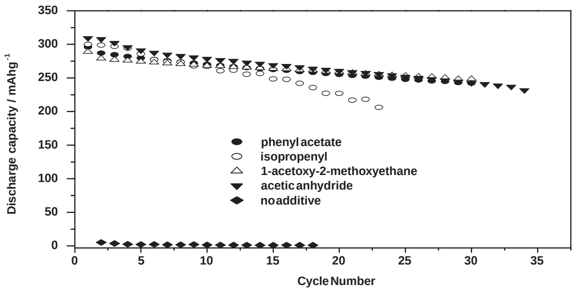


Figure 2. Capacity vs cycle number for Li/MCMB6-28 in 1 M $LiPF_6$/PC-DMC (1:2 v/v) in 1 wt % different additives.

tively. Likewise, additives AME and AA have short plateaus with low irreversible capacity of 92 mA h g^{-1} and 71 mA h g^{-1}, respectively.

Figure 2 shows the cycle performance of the electrolyte containing different additives, AME, AA, and PA additives have shown good capacity retention and additive isopropenyl acetate has the least capacity retention.

Figure 3 shows the plot of LUMO energy of additives succinimide,[6] vinyl,[5] and acetate group vs reduction potential obtained from the cyclic voltammogram. The rough linearity obtained is consistent with the assumption that additives with low LUMO energy than the electrolyte solvent should have high reduction potential in order to suppress the electrolyte decomposition. Therefore, molecular orbital theory can be applied as a rule of thumb for the selection of the additive precursors. The components of SEI film could also play a very vital role in determining the electrochemical performance.[3]

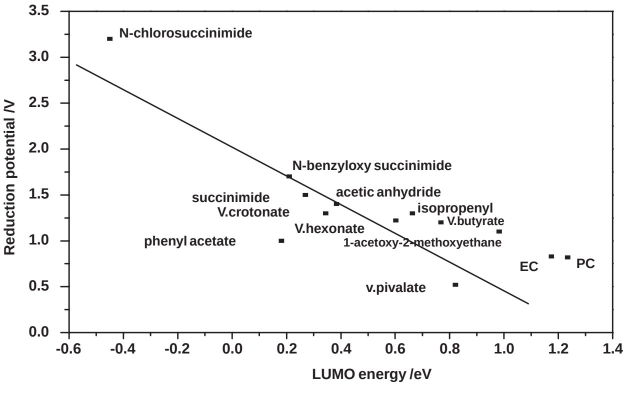


Figure 3. Relation between LUMO energy and reduction potential of acetate, vinyl, and succinimide group compounds.

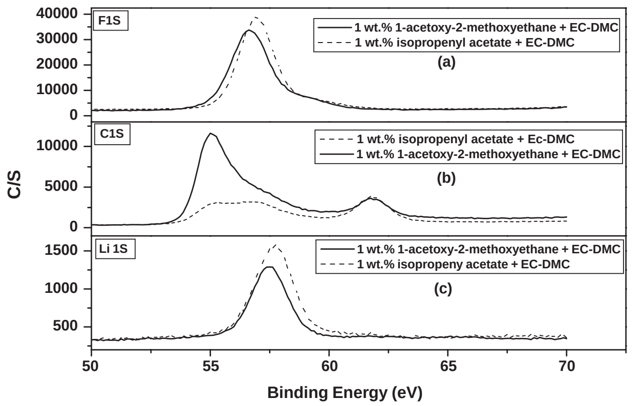


Figure 4. X-ray photoelectron spectroscopy (XPS) of SEI film surface of 1 wt % isopropenyl acetate and 1-acetoxymethoxy ethane in 1 M $LiPF_6$/EC-DMC (1:2) (a) fluorine, (b) carbon, and (c) lithium.

Figure 4 shows SEI film components formed as a result of the addition of the additives IPA and AME determined by XPS (ESCA 500). In the case of IPA additive the amount of inorganic components such as lithium and fluorine are higher and organic components such as carbon and oxygen are lesser in amount than the additive AME, it might be the reason for the bad cycle performance shown by the additive IPA. The impedance values are 190, 18.5, 12.0, and 15.0 Ω for IPA, AME, PA, and AA, respectively. The high impedance value in the additive IPA may be due to the higher amount of inorganic components and lower carbon contained in the SEI film,[3,9–13] which causes instability of the SEI film.

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