

Studies of the Passivation Film as a Function of the Concentration of Electrolyte in Lithium-ion Battery

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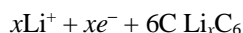
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The irreversible capacities caused by the reduction of solvent on the surface of a negative electrode (KMFC: Kawasaki Mesophase Fine Carbon) were examined during the initial cycle in ethylene carbonate (EC)-diethyl carbonate (DEC) electrolyte solutions at various concentrations of LiPF₆. Chronopotentiograms, linear sweep voltammograms, and impedance spectra clearly showed differences in irreversible capacity and that those differences are related to the concentration of electrolyte during the initial charge. These differences were caused by the amount of solvent decomposition as a function of the concentration of LiPF₆ electrolytic salt. The data are discussed with reference to the concentration of electrolytic salt and the properties of passivation film formed by solvent decomposition.

Keywords : Passivation film, Lithium ion battery.

Introduction

A considerable interest exists in lithium-carbon intercalation compounds, for use as anode materials for lithium (Li)-ion batteries.¹⁻¹⁰ These materials show excellent cycling properties and improved safety compared to the rechargeable Li metal battery. Studies of the intercalation of Li in graphite have generally concluded² that the stoichiometry range corresponds to Li_xC₆, where 0 < x < 1 according to the equation below;



This corresponds to a theoretical specific charge of 372 mAh/g. One of the problems which arises from the use of carbon anodes is the irreversible reaction, which occurs during the first charging-discharging cycle. The capacity associated with this related to the irreversible reaction is unusable, since the Li which is consumed in the initial charge cannot be recovered.

It is widely recognized that part of the irreversible capacity arises from the reduction of solvent, followed by the formation of a passivation film or a solid electrolyte interface (SEI) on the carbon surface.^{3,4,7-10} The film, which is ionic conducting and an electronic insulating, is capable of blocking the further reduction of solvent while allowing Li-ion insertion so that the side reactions are suppressed after the initial charge. The growth and properties of the passivation film are dependent on the electrolyte composition and additives. Therefore, using appropriate solutions and additives makes it possible to extend the cycle life of carbon electrodes. Several reports have appeared which concluded that ethylene and diethyl carbonates (EC-DEC) might be a superior solvent system for Li ion batteries with carbon electrodes.^{5,6} In this case, it is well known that the passivation film is formed by the reduction of solvent on the surface of

the carbon electrode to form Li₂CO₃.^{11,12}

In this paper, the irreversible properties caused by the reduction of solvent on the surface of the negative electrode (KMFC: Kawasaki Mesophase Fine Carbon) were examined during the initial cycle in ethylene carbonate (EC)-diethyl carbonate (DEC) electrolyte solutions with various concentrations of LiPF₆. Chronopotentiograms, linear sweep voltammograms, and impedance spectra were studied in order to understand the irreversible capacity related to the concentration of electrolyte during the initial charge.

Experimental Section

Kawasaki mesophase fine carbon (KMFC) electrodes were prepared by mixing KMFC powder (Petoca Co. Ltd.) with polyvinylidene fluoride (PVDF: Kureha Co. Ltd.) as a binder, followed by pressing on to a copper foil. After vacuum drying at 120 °C for 6 hours, the electrodes were placed in three-electrode cells under an atmosphere of argon. Lithium metal was used as both the counter and the reference electrodes. The reference electrode was sandwiched between a square KMFC electrode (1 cm × 1 cm) and a Li counter electrode, which were separated by a polypropylene (Celgard #2500) separator. The cycling tests of the KMFC electrode were carried out using the WBCS3000 battery cycle system. The electrochemical properties of the passivation film on the KMFC were investigated in an organic electrolyte system. High-purity ethylene carbonate (EC) and 1,2-diethyl carbonate (DEC) (Mitsubishi Chemical, battery grade) were used as solvents for the electrolyte solution. Lithium hexafluoro phosphate, LiPF₆ (Morita Chemical Industry) was used as the electrolytic salt. Various concentrations of electrolytes (0.50, 0.75, 1.00, 1.25, and 1.5 M) of LiPF₆ were prepared under an argon atmosphere.

The properties of the passivation film on the KMFC and

the first intercalation of Li^+ in KMFC through the passivation film were investigated by chronopotentiometry, linear sweep voltammetry, and a.c. impedance spectroscopy by means of a Potentiostat/Galvanostat (EG&G model 273A) and a Lock-in Amplifier (EG&G model 5210). After charging the KMFC electrode until 0.6 V and 0 V (vs. Li/Li^+), the open-circuit potential was measured and an impedance measurement was performed by applying the previously measured open-circuit potential, overlaid with a 5 mV harmonic perturbation signal in the frequency range of 100 kHz to 10 mHz.

Results and Discussion

Figure 1 shows typical voltage-capacity profiles of the KMFC electrode at a low rate of $0.5 \text{ mA}/\text{cm}^2$ in 1 M $\text{LiPF}_6/\text{EC}:\text{DEC}$ (1 : 1, volume ratio). The voltage on the first charge rapidly decreased from an open-circuit voltage (OCV) to 0.5 V (vs. Li/Li^+). This region (A in the insert in Figure 1) can be attributed to the film formed as the result of the solvent reduction. The decomposition reaction of EC and DEC was completed above 0.5 V. The other part, below 0.5 V, represents lithium intercalation into KMFC electrode through the film. The physical and chemical structures of the film have been described in detail in ref. 9. This film was not produced on the second charge since the film blocked any further solvent reduction. Generally, the origins of the irreversible capacity of carbon electrode are attributed to,^{8,9} i) the reduction of the solvent on carbon electrode surface, ii) the irreversible insertion of lithium into the carbon structure, iii) and so on. Our previous studies have confirmed that the above two reasons represent major factors of initial irreversible capacities. The total irreversible capacity was calculated

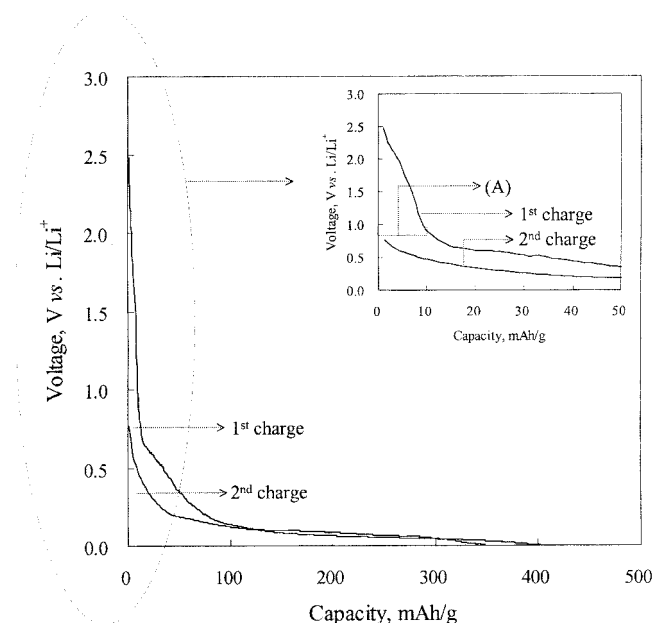


Figure 1. Voltage-capacity profile of a KMFC electrode in 1 M $\text{LiPF}_6/\text{EC}:\text{DEC}$ (1 : 1, volume ratio); Current density is $0.5 \text{ mA}/\text{cm}^2$.

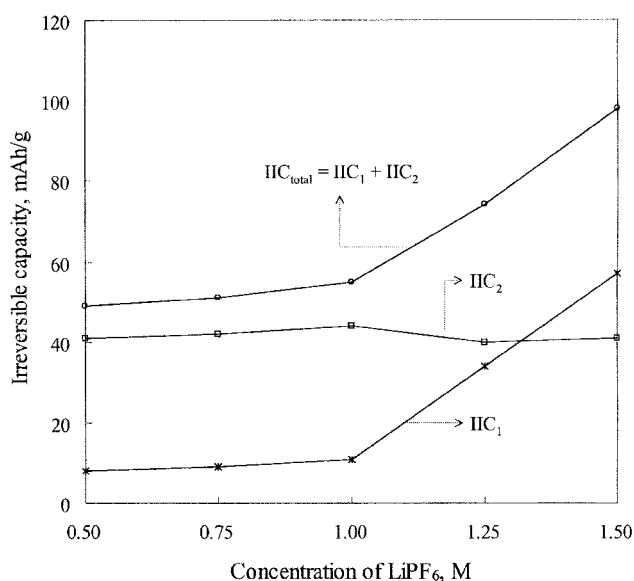
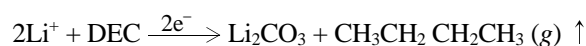
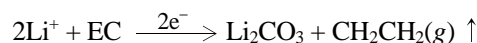


Figure 2. Plots of initial irreversible capacities vs. concentration of LiPF_6 in the electrolyte.

by subtracting the second charge capacity from the initial charge capacity. The initial irreversible capacity (IIC) is characterized as the summation of those caused by the reduction of solvent (IIC_1) and the initial irreversible capacity caused by the irreversible insertion of lithium into KMFC (IIC_2). Figure 2 presents the initial irreversible capacities as a function of concentration of LiPF_6 . The IIC_1 increased from 10 mAh/g to 52 mAh/g by increasing the concentration of LiPF_6 from 0.5 M to 1.5 M. The stoichiometry for the involvement of Li ion in electrolyte with the reduction of solvent¹³ is as follows;



From above equation, the amount of the solvent decomposition increases with increasing Li^+ in electrolyte solution. Therefore, the amount of the solvent decomposition is a function of LiPF_6 concentration. The variation of IIC_2 as the LiPF_6 concentration is very small when it was compared with IIC_1 , which shows a minor effect of electrolyte concentration on the irreversible insertion of Li into KMFC. The main tendency of total initial irreversible capacity follows the IIC_1 caused by solvent reductions.

Figure 3 shows a typical equivalent circuit and an impedance spectrum measured on the charged KMFC electrode in 1 M $\text{LiPF}_6/\text{EC}:\text{DEC}$ electrolyte. The equivalent circuit was adopted from B. Markovsky *et al.*¹⁴⁻¹⁶ The symbols R_{sol} , R_f , R_{ct} , C_f , C_{dl} , and Z_w denote the solution resistance, film resistance, charge transfer resistance, film capacitance, double layer capacitance, and the Warburg impedance, respectively. The high frequency semicircle in the impedance spectrum can be attributed to the migration of Li^+ through the film, which covers the KMFC electrode. The medium frequency semicircle is assigned to the Li^+ charge transfer in the film-

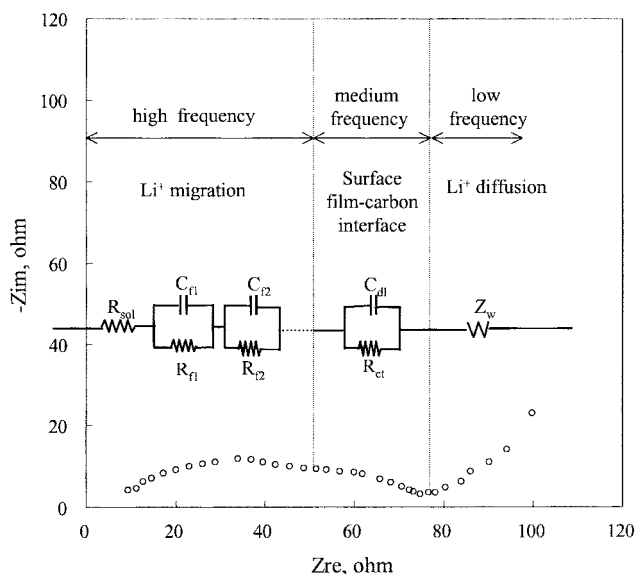


Figure 3. Typical equivalent circuit and an impedance spectrum of a KMFC electrode after charging until 0.0 V (vs. Li/Li^+).

KMFC interface. The solid-state diffusion of Li^+ in the KMFC layer explains the sloping line at the low frequencies. We focused on the film resistance at high frequency (100 kHz to 10 Hz), in order to investigate the properties of the initial irreversible capacity, which is concerned with solvent decomposition by using the non-linear-least-squares (NLLS) fitting program.

Figure 4 shows impedance spectra of the KMFC electrode in x M $LiPF_6/EC : DEC$ (1 : 1) after charging to 0.5 V (vs. Li/Li^+). The film resistances were increased from 195 to 260 Ω as the concentration of electrolytic salt was increased from 0.5 M to 1.5 M. However, the film resistance can be

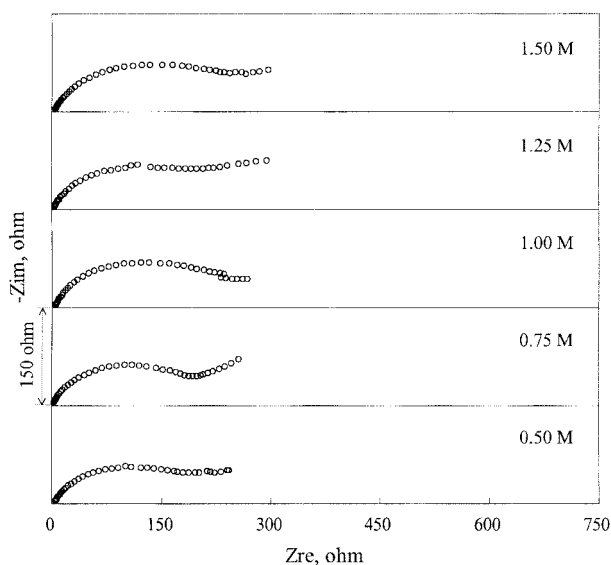


Figure 4. Impedance spectra of KMFC electrode after charging from 0.5 V (vs. Li/Li^+) in x M $LiPF_6/EC : DEC$ (1 : 1); x is 0.50, 0.75, 1.00, 1.25, and 1.50. Frequency ranges are from 100 kHz to 10 Hz.

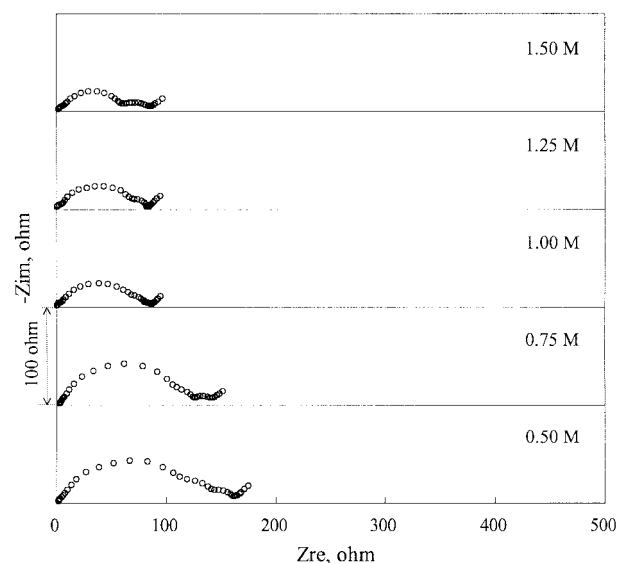


Figure 5. Impedance spectra of a KMFC electrode after charging from 0.0 V (vs. Li/Li^+) in x M $LiPF_6/EC : DEC$ (1 : 1); x is 0.50, 0.75, 1.00, 1.25, and 1.50. Frequency ranges are same as Figure 4.

changed as further charging occurs. Figure 5 shows impedance spectra of the KMFC electrode measured after charging completely from 0.0 V. As a result, the film resistances were decreased with levels of Li^+ in the electrolyte. Figure 6 summarizes the dependence of film resistance on the concentration of $LiPF_6$ in the electrolyte solution. $R_{f(0.5 V)}$ and $R_{f(0.0 V)}$ are film resistances measured after charging until 0.5 V and 0.0 V, respectively. The film resistance measured after charging until 0.5 V was proportionally increased as the concentration of $LiPF_6$. As worded at Figure 2, the amount of the solvent decomposition is a function of $LiPF_6$ concentration. The thickness of passivation film is increased in proportion to the amount of the solvent decomposition. And also Li insertion into the film is not occurred at the potential

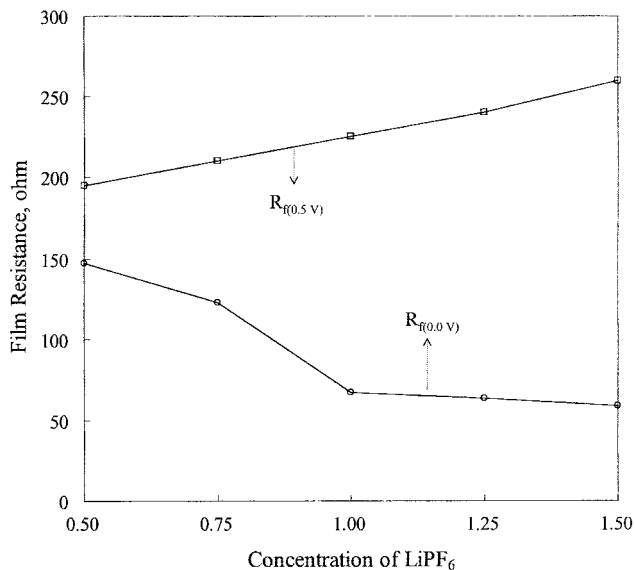


Figure 6. Plots of film resistance vs. concentration of $LiPF_6$ in electrolyte at different charging voltages.

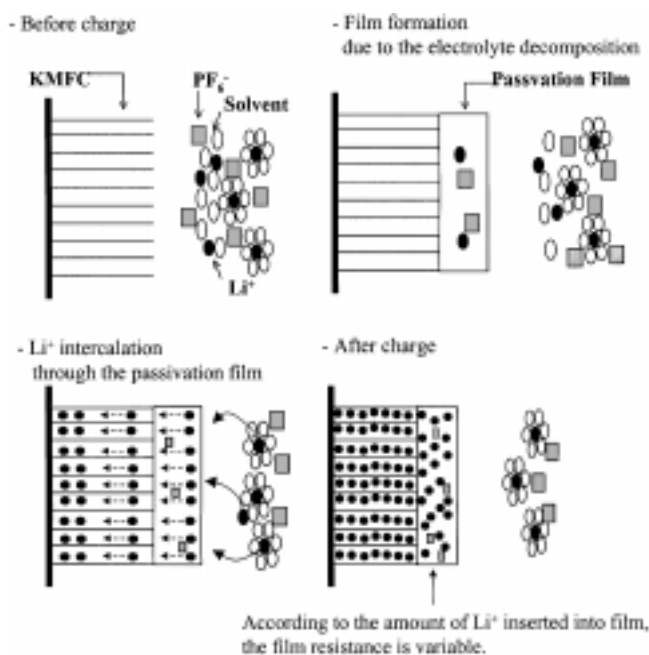


Figure 7. Schematic description of an initial charging mechanism.

range above 0.5 V. Accordingly, Li is not in the film when the KMFC electrode is charged until 0.5 V. Therefore, it may be thought that the film resistance was increased as the amount of solvent decomposition. However, the film resistance after charging until 0.0 V was decreased as the amount of Li^+ in electrolyte. It is likely that Li^+ is intercalated into KMFC through the film from below 0.5 V and then Li^+ is inserted into the film. The resistance of the film. Therefore, the film resistance is decreased with the amount of Li^+ inserted into the passivation film during charging process to 0.0 V.

To summarize above data, Figure 7 shows a schematic description of the initial charge mechanism on the negative electrode. Before the charge, Li^+ , which is solvated by the solvent is distributed in the electrolyte solution. During the initial charge, the passivation film is formed on the surface of the KMFC electrode as the result of solvent decomposition ($> 0.5 \text{ V vs. Li/Li}^+$). Therefore, when the cell was charged until 0.5 V, the variation of the film resistance ($R_{f(0.5 \text{ V})}$) was increased as the amount of solvent decomposition which was related to LiPF_6 concentration. Under the Li^+ intercalation voltage ($< 0.5 \text{ V vs. Li/Li}^+$), Li^+ is inserted into the passivation film and is then intercalated into the KMFC electrode through the film. After charging, Li^+ is located in the KMFC layer and in the passivation film. Especially, Li^+ remained in the film make a change the film resistnace. Therefore, the properties of the film are variable dependent of the level of Li^+ inserted into the film. In other words, as the amount of Li^+ inserted into the passivation film is larger, the resistance of film is decreased. Due to the reason, the variation of the film resistance ($R_{f(0.0 \text{ V})}$) was decreased when the cell was charged until 0.0 V.

Linear sweep voltammetry (LSV) was performed, in order to understand the properties of the passivation film formed at

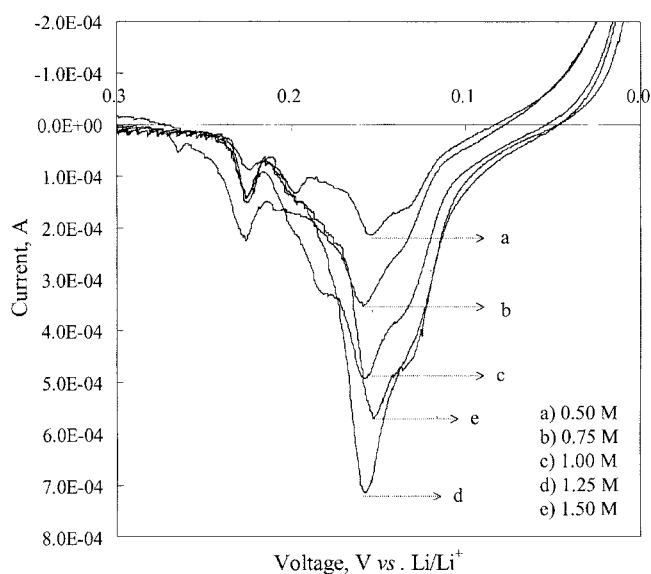


Figure 8. Linear sweep voltammograms of Li^+ deintercalation after charging until 0.0 V; scan rate is $5 \mu\text{V/sec}$.

various concentrations of LiPF_6 . Using LSV, anodic peak potentials were investigated at the discharging process. The anodic peak potential must be more negatively shifted, in order to obtain a high output voltage for Li-ion batteries. Figure 8 shows the LSV of Li^+ deintercalation at a scan rate of $5 \mu\text{V/sec}$. The shift of anodic peak potentials of the initial Li^+ deintercalation is unclear depending upon the concentration of LiPF_6 . Figure 9 shows the LSV for the deintercalation of Li^+ , at a scan rate of $100 \mu\text{V/sec}$. The negative peak shift of anodic peak potentials of the initial Li^+ deintercalation with an increase in the concentration of LiPF_6 can be clearly observed. This shift is related to the film resistance (R_f) (see Figure 5, 6). 1.50 M LiPF_6 electrolyte had the lowest value for R_f after initial charging from 0.0 V (Figure 5) and, as a result, the anodic peak potential of the electrolyte is

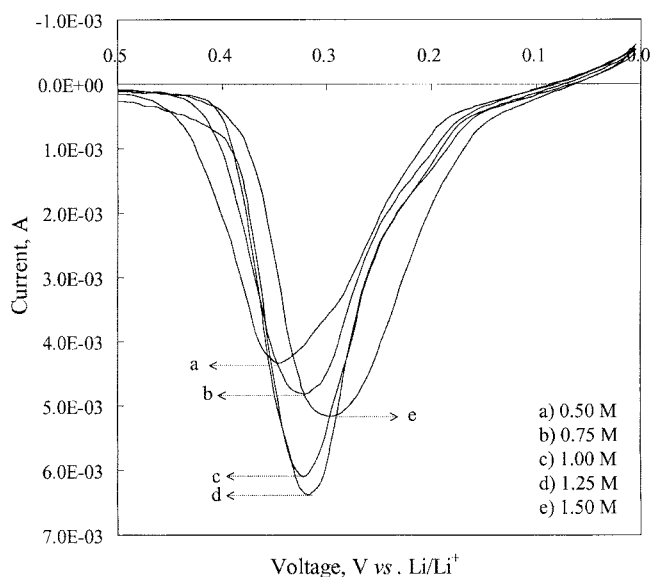


Figure 9. Linear sweep voltammograms of Li^+ deintercalation after charging until 0.0 V; scan rate is $100 \mu\text{V/sec}$.

more negatively shifted than any other electrolytes in Figure 9. The 0.50 M electrolyte had the largest value of R_f after an initial complete charging and now has the most positive anodic peak potential. I can therefore conclude that a higher output voltage can be available for Li-ion batteries as the concentration of Li ion in the electrolyte increases. However, since 1.00 M and 1.25 M electrolytes have a higher anodic current density than a 1.50 M electrolyte, an optimum concentration should be chosen for an actual Li battery system.

Conclusions

Relationships between the concentration of the LiPF_6 electrolytic salt and the properties of passivation film, formed by solvent decomposition have been investigated. The initial irreversible capacity was the result of solvent decomposition up to 0.5 V and the irreversible insertion of lithium into KMFC under 0.5 V. From the initial charging curves, the amount of the solvent decomposition reaction was a function of the concentration of LiPF_6 in the electrolyte solution. Based on impedance data, the properties of the passivation film were also changed as a function of the amount of Li^+ inserted into the film. The anodic peak potentials of the initial discharge were negatively shifted with decreasing film resistance, since the amount of Li^+ inserted into the film was increased. We concluded that the initial irreversible capacity in the Li battery could be reduced by selecting an optimum concentration of electrolytes which controls the solvent decomposition reaction.

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