Correlation between Co-intercalation of Solvents and Electrochemical Intercalation of Lithium into Graphite in Propylene Carbonate Solution

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In lithium ion batteries, highly graphitized carbonaceous materials have been extensively studied as negative electrodes because of their acceptable high capacity, very flat potential as low as Li metal, etc. One of the problems for graphite negative electrode is irreversible capacity due to electrolyte decomposition and subsequent formation of surface film, namely SEI, in the initial stage of charge and discharge cycling.

The present authors have done the *in-situ* electrochemical STM and AFM observation of the basal plane of graphite in 1 mol dm^{-3} LiClO$_4$ / EC - DEC and other solvents.[1-5] They supported the surface film formation mechanism proposed by Besenhard et al.[6] that the surface film is formed on graphite through the co-intercalation of solvent with Li$^+$ ion. To further clarify the role of co-intercalation of solvated Li$^+$ ion on the SEI film formation, co-intercalation of solvent into graphite should be studied in advance.

In this paper, correlation between co-intercalation of solvents DMSO, 2-MeTHF, dimethoxymethane (DMM), diethoxymethane (DEM), 1,2-diethoxyethane (DEE) and 1,2-dibutoxyethane (DBE)) and electrochemical intercalation of Li$^+$ ion into natural graphite in propylene carbonate solution (PC) containing 1.0 mol dm^{-3} LiClO$_4$ in the presence of various amounts of these solvents was investigated.

Co-intercalation of the above solvents with Li$^+$ ion into natural graphite flakes was studied by a solution method.[7,8] The electrolytes of 1 mol dm^{-3} LiClO$_4$ / PC containing 0.5, 1.0, 2.0 and 4.0 mol dm^{-3} DMSO, 2-MeTHF, DMM, DEM, DEE, and DBE were prepared. Electrochemical properties of natural graphite powder (NG7) in the PC-based electrolytes were studied by charge and discharge measurements using a three-electrode cell. Solvent's ability to solvate Li$^+$ ion was studied by theoretical calculation.

Result of co-intercalation was given in Table 1. As is clear from Table 1, DMSO, DMM, DEM, and DEE co-intercalate into graphite with Li$^+$ ion to form ternary Li-solvent-GICs, while no co-intercalation of 2-MeTHF and DBE took place to give binary Li-GICs. Considering the values of ΔH in Table 1, the solvation abilities are in the order of DBE > DEE > DEM > DMSO > DMM ≈ PC > 2-MeTHF. Although Li$^+$ ion in the present electrolytes should be solvated with more than two solvent molecules, solvation abilities given by Table 1 are qualitatively useful. Except for 2-MeTHF, the values of ΔH of co-solvents are larger than that of PC, indicating that preferred solvation toward Li$^+$ ion should take place in the binary PC-based electrolytes in this study.

Figure 1 shows the voltage profile of the first charge-discharge cycle for graphite electrode in 1 mol dm^{-3} LiClO$_4$ / PC containing 0.5 mol dm^{-3} DMSO. In the present PC-DMSO system, Li$^+$ ion should be preferentially solvated by DMSO due to its higher electron donicity than that of PC. As is clarified by the solution method, DMSO co-intercalates into graphite. In

the presence of DMSO in PC, Li$^+$ solvated by DMSO intercalates into graphite first and then thus reductive decomposition of DMSO solvating Li$^+$ between graphite layers gradually occurs, leading to the formation of the stable surface film.

The chronopotetiometric profile of graphite in 1 mol dm^{-3} LiClO$_4$ / PC containing DBE and 2-MeTHF only showed large potential plateau at around 0.85 V vs. Li / Li$^+$. This result is very similar to the chronopotetiometric profile of graphite in 1 mol dm^{-3} LiClO$_4$ / PC.

From the results obtained above, the co-intercalation of solvent should be the first step for the formation of SEI in the present system

References
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Table 1 Results of co-intercalation studied by solution method and heats of reaction determined by density functional theory

Solvent	Co-intercalation	Heats of Reaction (ΔH) (kcal /mol)*
DMSO	◯	- 56.2
2-MeTHF	X	- 45.1
DMM	◯	- 51.9
DEM	◯	- 58.9
DEE	◯	- 65.1
DBE	X	- 66.9
cf) PC		- 51.8

* Heats of reaction (Li$^+$ + solvent = Li$^+$-solvent) at 298.15 K were obtained by $\Delta H = H(\text{Li}^+\text{-solvent}) - \{H(\text{solvent}) + H(\text{Li}^+)\}$.
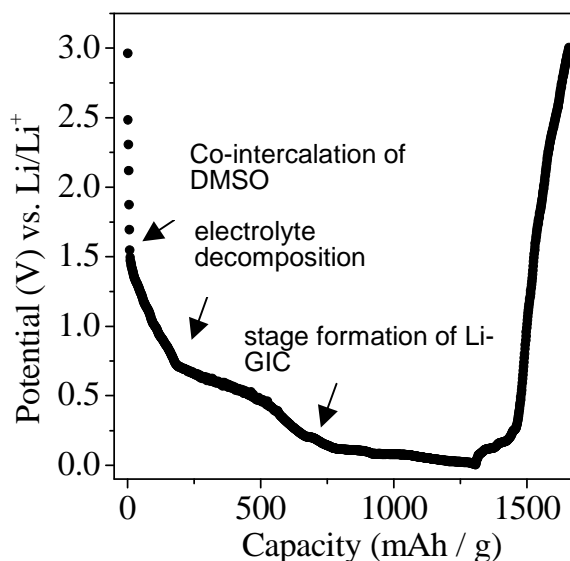

Fig. 1. Voltage profile of the first cycle for graphite electrode in 1 mol dm^{-3} LiClO$_4$ / PC containing 0.5 mol dm^{-3} DMSO.