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Short communication

Reactions of metallic Li or LiC_6 with organic solvents for lithium ion battery

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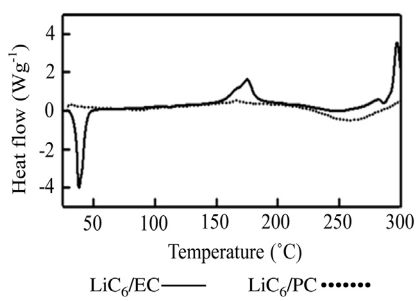
HIGHLIGHTS

- EC more easily reacts with metallic Li and LiC_6 than PC.
- EC more easily forms lithium alkyl carbonate than PC.
- DEC, EMC and DMC react with Li in the same manner.

GRAPHICAL ABSTRACT



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ABSTRACT

DSC (Differential Scanning Calorimetry) study has been made on the reactions of metallic Li or LiC_6 with organic solvents for lithium ion battery. Ethylene carbonate (EC) more easily reacts with metallic Li and LiC_6 than propylene carbonate (PC). This may be because formation of lithium alkyl carbonate is more difficult for PC than EC. On the other hand, diethyl carbonate (DEC), ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC) react with Li in the same manner. Reactions of Li and LiC_6 with organic solvents have been discussed based on the results of quantum calculation.

1. Introduction

Since lithium ion battery uses flammable organic solvents, there is a possibility of firing or explosion of the battery at high temperatures, by short circuit formation, by overcharging and so on. High safety is required to avoid these accidents especially for the application to the electric sources of hybrid cars and electric vehicles. Thermal stability of lithium ion battery is therefore an important research subject. In our group, the effect of organofluorine compounds on the thermal stability and electrochemical properties of graphite has been investigated in ethylene carbonate (EC)-based and propylene carbonate (PC)-mixed electrolyte solutions [1–5]. It has been found that mixing of fluorine compounds effectively improves thermal and oxidation stability of electrolyte solutions. This would be attributed to the low reactivity of with Li and high oxidation stability of fluorine compounds [5]. It was already reported that EC, dimethyl carbonate (DMC), ethyl methyl carbonate (EMC) and diethyl carbonate (DEC) react with Li, yielding lithium alkyl carbonates such as $(CH_2OCO_2Li)_2$ and $ROCO_2Li$ (R: CH_3, C_2H_5) [6–11]. Reduction mechanisms of these solvents were also

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reported [9–11]. Li-intercalated graphite, LiC_6 starts to decompose above ca. 100 °C [7]. Therefore exothermic peaks due to the reactions of LiC_6 with organic solvents and solid electrolyte interphase (SEI) are observed above 130 °C in DSC (Differential Scanning Calorimetry) study [3–5,7]. Thermal decomposition of electrolyte solutions and SEI takes place at higher temperatures than ca. 200 °C [3–5,7,12–18]. This means that the reactivity of Li with organic solvents is important because it occurs at lower temperatures than those for thermal decomposition of electrolyte solutions and SEI. In this paper, the reactivity of metallic Li and LiC_6 with organic solvents is reported.

2. Experimental

DSC measurement was carried out using a mixture of metallic Li or LiC_6 and EC, PC, DEC, EMC or DMC between room temperature and 300 °C at a temperature increasing rate of 5 °C min^{-1} (DSC-60, Shimadzu). Sample mixtures were sealed in aluminum cell for DSC in a glove box. Lithiated graphite samples were electrochemically prepared in 1 mol L^{-1} $LiPF_6$–EC/DMC (1:1 vol.) after 2 cycles. Host graphite was natural graphite powder (purity: >99.95%) with average particle size of 10 μm (NG10 μm). The d_{002} value obtained by X-ray diffractometry (XRD-6100, Shimadzu) was 0.3354 nm. Surface area and meso-pore volume obtained by BET surface area measurement (Tristar 3000, Shimadzu) were 9.2 m^2 g^{-1} and 0.035 cm^3 g^{-1}, respectively. D-band to G-band intensity ($R = I_D/I_G$) obtained by Raman spectroscopy (NRS-1000, Jasco) with Nd:YVO_4 laser (532 nm) was 0.23. Composition of Li-intercalated graphite samples was calculated from discharge capacity to be $Li_{0.85-0.99}C_6$. Lithiated graphite samples used for DSC measurements were 1.4–1.6 mg. Electrolyte solution and metallic Li were 3 μL and 9–11 mg, respectively. In the case of EC, 4 mg of solid EC was sealed in aluminum cell with metallic Li or LiC_6. To discuss about the reactions of Li with organic solvents, bond lengths and electrostatic charges of oxygen and carbon of organic solvent molecules were calculated by semi-empirical AM1 method using Spartan '06.

3. Results and discussion

Fig. 1 shows DSC profiles for a mixture of metallic Li and EC or PC. Endothermic peaks were observed at 38 and 182 °C, indicating the melting of EC and metallic Li, respectively. No exothermic reaction was observed below 182 °C probably because metallic Li was covered by thin oxide film which prevented the reactions of Li with EC and PC. As soon as metallic Li melted, reaction of Li with EC started, giving an exothermic peak at 217 °C. On the other hand, PC is more stable than EC against Li. The reaction of Li with PC started at 234 °C and its peak position was situated at 257 °C. Fig. 2 shows DSC curves for mixtures of metallic Li and DEC, EMC or DMC. Strong

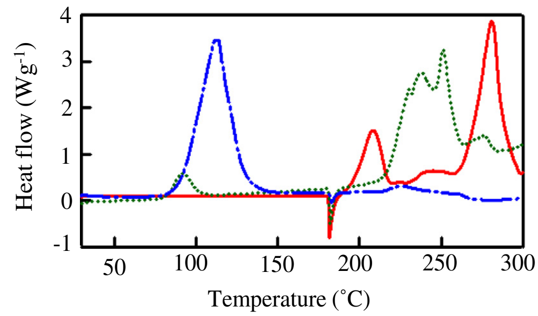

Fig. 2. DSC curves for mixtures of metallic Li and DEC, EMC or DMC. Li/DEC ——•——•——, Li/EMC ··········, Li/DMC ————————.

exothermic peak for Li/DEC mixture started to increase at 80 °C. This would be due to the reaction of Li with DEC, being different from another reaction such as decomposition of Li/DEC complex, which would be an endothermic reaction like the dissociation of $LiPF_6$ to LiF and PF_5. Weak exothermic peak for Li/EMC mixture also started at 80 °C. Exothermic peaks were located at 112 °C and 92 °C below the melting point of Li for DEC and EMC, respectively, while several peaks were found above 180 °C for DMC. This may be attributed to the lower surface tensions of DEC, EMC and DMC than those of EC and PC (DEC: 24.5, (40 °C) and 18.0 mN m^{-1} (100 °C) [19], DMC: 26.3 (39 °C) and 17.8 mN m^{-1} (100 °C) [20], EC: 42.2 mN m^{-1} (40 °C), PC: 39.6 mN m^{-1} (40 °C)). Additionally the boiling points of DEC, EMC and DMC are 127, 107 and 90 °C, respectively [21]. Therefore DMC and most of EMC vaporize before reacting with Li. However, DEC having the higher boiling point is able to permeate through the crack of surface oxide film of Li due to its lower surface tension, giving an exothermic peak at 112 °C by the reaction with Li. Some exothermic peaks by the reaction with Li and thermal decomposition were observed between 200 and 300 °C for EMC and DMC.

Reactions of LiC_6 with organic solvents gave different DSC profiles as shown in Figs. 3 and 4. Li-intercalated graphite, LiC_6 decomposes above 100 °C, releasing fresh Li [7]. Fig. 3 indicates that EC reacted with Li deintercalated from graphite, giving an exothermic peak at 174 °C while PC did not exhibit an exothermic peak up to 300 °C. On the other hand, DEC, EMC and DMC showed the similar DSC curves to each other, providing exothermic peaks due to the reactions with deintercalated Li at 130–135 °C. Exothermic peaks above 250 °C may be due to thermal decomposition of organic solvents and SEI.

Lithium alkyl dicarbonate, $(CH_2OCO_2Li)_2$ is experimentally confirmed main product by the reaction of EC with LiC_6 [6–11]. The formation of $(CH_2OCO_2Li)_2$ may consist of two step reactions. The

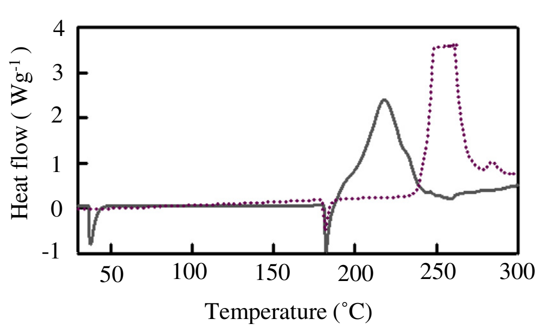

Fig. 1. DSC curves for mixtures of metallic Li and EC or PC. Li/EC ————————, Li/PC ··········.

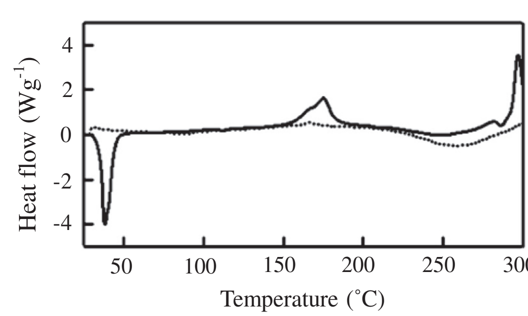

Fig. 3. DSC curves for $Li_{0.99}C_6$/EC and $Li_{0.96}C_6$/PC mixtures. $Li_{0.99}C_6$/EC ————————, $Li_{0.96}C_6$/PC ··········.