

Short communication

The effect of various electrolyte additives on reversible Li-graphite intercalation

D.L. Foster ^{*}, W.K. Behl, J. Wolfenstine

U.S. Army Research Laboratory, 2800 Powder Mill Road, Adelphi, MD 20783-1197, USA

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It is known that when lithium is intercalated into graphite in pure propylene carbonate (PC) based electrolytes, solvent cointercalation occurs leading to the destruction of the graphite structure (i.e., exfoliation) [1–6]. In order to overcome this problem, PC can be mixed with other solvents such as ethylene carbonate (EC) [3–6] or a chelating agent such as crown ether can be added to PC [1,4,5]. It has been suggested that electrolytes containing EC form a stable passivating layer, that retards cointercalation of solvent into graphite [4–6], whereas electrolytes containing a crown ether additive limit the cointercalation by excluding the solvent molecules from the graphite layers until a passivating layer is formed from reduction of the solvent on the graphite surface [4]. Recently, it was shown [7,8] that graphite can be reversibly cycled in a PC electrolyte by first cycling the graphite electrode once in a EC or dimethyl carbonate (DMC) based electrolyte and then transferring the electrode to a PC based electrolyte. The first cycle in the EC or DMC based electrolyte forms an impermeable passivating layer that prevents PC cointercalation after moving the electrode to the PC based electrolyte. Additional cycling increases the thickness of the passivating layer [8–10]. In these studies only LiClO₄ solute was used. It is of interest to investigate what happens when a graphite electrode is cycled once in an electrolyte with PC solvent containing a chelating additive such as crown ether and then transferred to a PC based electrolyte without additive. Will there be an impervious passivating layer formed on the graphite surface? It is the purpose of this note to answer this question as a function of chelating agent and electrolyte salt.

Three different chelating agents were used: (1) tertiary polyamine, *N,N,N',N',N'*-pentamethyldiethylenetriamine, PMDT (Aldrich), (2) 12-Crown-4 (Aldrich) and (3) tetraglyme (Aldrich). These chelating agents were chosen because they all showed an increase in ionic conductivity when added to PC [11]. Propylene carbonate (Grant) and the chelating agents were dried over 4 Å molecular sieves and verified by Karl-Fischer coulometric titration to have moisture concentration of less than 20 ppm before use. Two different salts were used: (1) LiPF₆ (Hashimoto, Japan) and (2) LiClO₄ (Aldrich). LiPF₆ was used as received. LiClO₄ was outgassed under vacuum at 150°C. SFG-44 graphite (Timcal) was used as received. Graphite electrodes were doctor bladed on electrodeposited copper (All Foils) foil substrates using a 5% poly vinylidene fluoride (PVDF) binder. The graphite electrodes were vacuum dried at 120°C for 24 h before use. Lithium intercalation and deintercalation in the graphite electrodes was carried out by cycling graphite flag electrodes vs. lithium electrodes in sealed glass cells in a glove box with a moisture and oxygen content of < 1 ppm. The cells were cycled at a current density of 28 μA/cm². The graphite electrodes were given one cycle in a 1 M salt:1 M chelating agent/PC solution then moved to the same electrolyte without the additive and cycled again.

The results for 1 M LiPF₆:1 M PMDT/PC are shown in Fig. 1. From Fig. 1 it is observed that no reversible lithium capacity is obtained. This result suggests that a protective film is not formed and thus, PC cointercalation occurred leading to extensive exfoliation of the graphite. Similar behavior is observed when using PC as a single solvent [1–6]. Switching the salt to LiClO₄ gave the same results as shown in Fig. 1.

The results for the first cycle in 1 M LiPF₆: 1 M 12-Crown-4/PC (solid line) and after the graphite elec-

^{*} Corresponding author. Tel.: +1-301-721-3429; fax: +1-301-721-3402; E-mail: dfoster@arl.mil

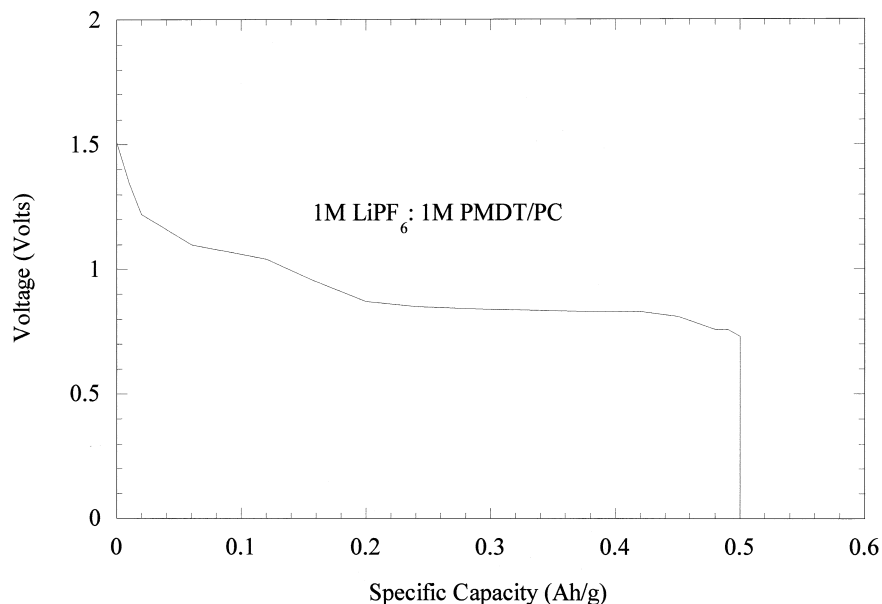


Fig. 1. Voltage vs. specific capacity for Li/graphite cell discharge in 1 M LiPF₆:1 M PMDT/PC.

trode was removed from the electrolyte and cycled once in electrolyte without the 12-Crown-4 additive (dashed line) are shown in Fig. 2. From Fig. 2, two important points are noted. Firstly, it is observed that reversible lithium intercalation is exhibited in the solution containing the 12-Crown-4 additive. This is in agreement with previous results [1,4,5]. Secondly, it is seen that the graphite electrode after being switched to the solution without the additive exhibited no reversible capacity. This suggests that after one cycle an impervious passivating layer does not form on the graphite in the 12-Crown-4 solution and hence, after switching the graphite electrode to PC based electrolyte

with no additive, the graphite electrode was destroyed by PC solvent cointercalation. A similar result to that observed in Fig. 2 was exhibited when LiClO₄ was used instead of LiPF₆. It is of interest to note that the results of the switching experiments are in contrast to the suggestions of others [4] who maintain that a stable passivating layer is formed in a 12-Crown-4/PC solution.

The results for the first cycle in 1 M LiPF₆: 1 M tetraglyme/PC (solid line) and after the graphite electrode was removed from the electrolyte and cycled once in electrolyte without the tetraglyme additive (dashed line) are shown in Fig. 3. From Fig. 3 it is observed that the

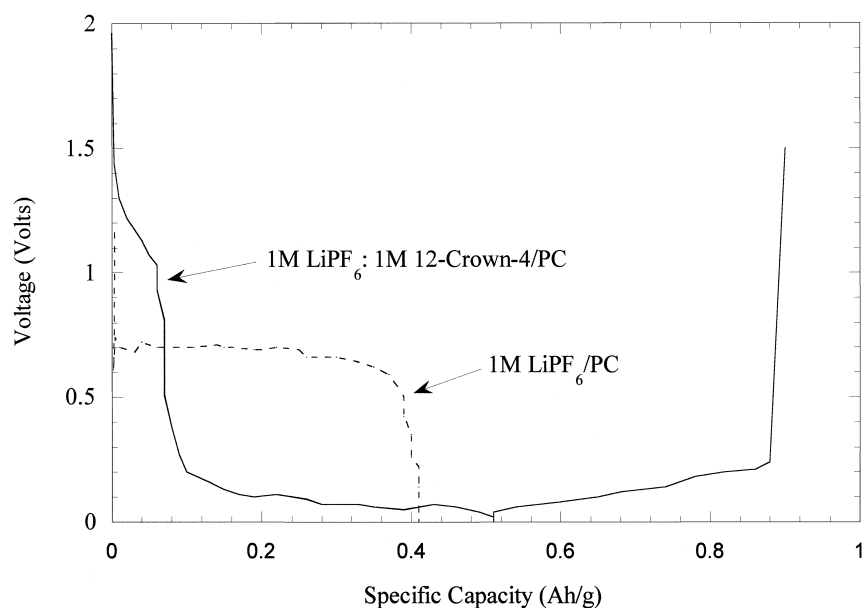


Fig. 2. Voltage vs. specific capacity for Li/graphite cell first cycled in 1 M LiPF₆: 1 M 12-Crown-4/PC (solid line) and then the graphite electrode is transferred to a 1 M LiPF₆/PC electrolyte and cycled again (dashed line).

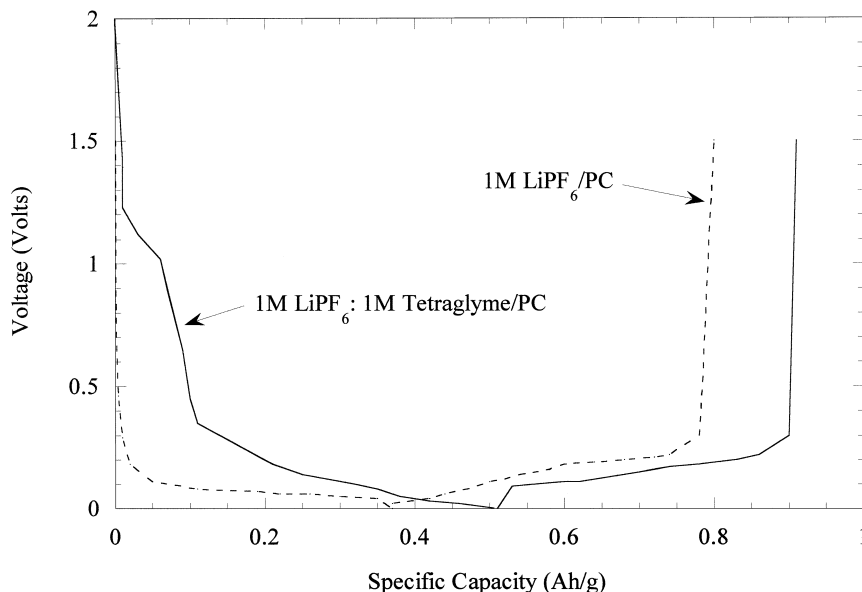


Fig. 3. Voltage vs. specific capacity for Li/graphite cell first cycled in 1 M LiPF₆: 1 M Tetraglyme/PC (solid line) and then the graphite electrode is transferred to a 1 M LiPF₆/PC electrolyte and cycled again (dashed line).

tetraglyme additive allows for reversible lithium intercalation. This is similar to the results for the 12-Crown-4 additive (Fig. 2, solid line). However, an important difference between the behavior of 12-Crown-4 and tetraglyme additives is that after subsequent switching the graphite electrode to the electrolyte solution without the additive, reversible lithium intercalation is observed only for the tetraglyme case. This suggests that graphite electrode is covered by a stable passivating layer during discharge in the 1 M LiPF₆:1 M tetraglyme/PC electrolyte which prevents solvent cointercalation when it is transferred to the electrolyte containing a salt and PC. Similar results to those shown in Fig. 3 were observed when LiClO₄ was used as the salt.

The results of this study reveal that out of the three chelating agents (PMDT, 12-Crown-4 and tetraglyme) investigated, only a PC based electrolyte containing tetraglyme forms a stable nonporous passivating layer on graphite during the first discharge. Because the layer is nonporous, lithium could be reversibly cycled into the graphite even after transferring the electrode into the PC based electrolyte without additive. The chelating agent 12-Crown-4, on the other hand, allows the reversible insertion of lithium into graphite from PC electrolytes on the first cycle even before a impermeable passivating film can be formed on the graphite surface. The film effectively passivates the preferred solvent reduction sites on the graphite surface but is sufficiently porous to allow PC to cointercalate into the graphite layers if the crown ether is removed from the solution. For the case of PMDT, the amine additive did not prevent cointercalation of PC on the first cycle leading to extensive exfoliation of the graphite.

The stability of the layers was independent of the salt type for LiPF₆ or LiClO₄. At present it is not known why the different additives exhibit a difference in behavior. Future work is underway to investigate this effect.

Acknowledgements

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