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The Role of Carbonate Solvents on Lithium Intercalation into Graphite

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Lithium intercalation into graphite was investigated using a graphite with a spheroidal particle morphology and propylene carbonate (PC)-based electrolytes containing LiPF₆, NaPF₆, or (C₄H₁₀)₄NPF₆ as the supporting electrolyte. The data from Li/C cells utilizing these electrolytes showed that reduction of PC on the graphite electrode occurs at about 0.9 V vs Li⁺/Li. The PC reduction potentials showed no dependence on the supporting electrolyte salt present in the electrolyte. Furthermore, there was no evidence of graphite exfoliation in PC electrolyte. This was supported by the observation that graphite electrodes retrieved from the Li/C cells, after PC reduction, and reassembled and tested with standard Li-ion battery electrolyte exhibited Li intercalation capacities identical to those exhibited by fresh graphite electrodes. The potentials at which PC is reduced are very similar to those previously found with graphite electrodes in which PC was reported to cointercalate into graphite as Li⁺(PC)_n, leading to its exfoliation at about the same potentials as found in this study. The data presented here are useful for the systematic design and optimization of electrolytes based on organic carbonate solvents to tailor Li-ion battery performance.
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Commercial Li-ion batteries use a carbonaceous material as the anode, LiPF₆ dissolved in mixtures of organic carbonate solvents as electrolytes, and a transition metal oxide (e.g., LiMn₂O₄, LiCoO₂, or LiNi_{1-(x+y)}Co_xMn_yO₂, etc.) as the cathode. Among the various types of carbonaceous materials, natural graphite is the most attractive anode because of its high theoretical specific capacity (372 mAh/g), abundance, and low cost.¹ The electrolyte solutions are reduced on the cathodically polarized graphite electrodes during initial charging of the Li-ion battery. Most of these reduction processes occur at potentials as high as 1.5 V above Li insertion into graphite² precipitate surface films, comprised of organic and inorganic Li salts,³ on the graphite particles. These surface films, called solid electrolyte interphases (SEI), which are Li-ion conducting but electronically insulating materials on which solvent reduction cannot be sustained, are needed for reversible lithium intercalation into the graphite electrode without the interference from solvent reduction.^{4,5} Ethylene carbonate (EC)-based electrolytes form a robust SEI that allows reversible Li intercalation into graphite according to the equation $\text{Li}^+ + \text{xe}^- + \text{C}_n \rightleftharpoons \text{Li}_x\text{C}_n$. Consequently EC is a component of all Li-ion battery electrolytes. It is well established that the Li insertion into graphite occurs in several stages, involving at least four phase transitions in the Li_xC_n materials at low potentials between 0.3 and 0.01 V vs Li/Li⁺, close to Li deposition potentials. In contrast to EC, if propylene carbonate (PC) is used as a single solvent for the electrolyte solution, the electrode potential during cathodic reduction in a Li/C cell becomes constant at around 0.9 V vs Li/Li⁺, indicating that reductive decomposition of PC takes place instead of Li intercalation.¹⁰ Different mechanisms have been proposed over the years to explain the inability to intercalate Li in to graphite when PC is used as the electrolyte solvent.^{6,11-18} A common opinion is that, in cases where the passivation by the surface films is not adequate, PC solvent molecules may cointercalate with Li⁺ into graphite to form the ternary intercalation compounds, Li_x(solv)_yC_n, at the relevant low intercalation potentials, after which the lattice structure of graphite may be destroyed by exfoliation of the graphene planes. Another prevalent opinion is that solvent molecules cointercalating with the Li⁺ even at potentials as high as 1 V vs Li/Li⁺ are reduced within the graphite, close to the surface of the particles, thereby blocking further Li⁺ insertion into the lattice. Chung et al.¹⁷ studied various types of graphites in EC/PC/(butylene carbonate (BC)-based electrolyte solutions and observed some capacity loss when cycled

in PC solutions. They concluded that the graphite exfoliation did not destroy the bulk structure completely, but rather caused significant changes on the graphite surface. Another opinion is that PC-based electrolytes do not form stable SEI compounds on the graphite surface.¹³ Aurbach et al. reported that the PC-based solvents do not involve complete exfoliation of the graphite particles, but rather cracking the electrode structure at a macroscopic level occurs, caused by the pressure of the gaseous product of PC reduction, propylene gas, generated continuously at the graphite edge planes.¹⁹ This occurs because of the poor passivation property of the reduction product of PC on the graphite surface. Despite the large body of work that exists on this subject, there is still a need to further understand the processes taking place on the graphite electrode in PC-containing electrolytes. For example, the absence of Li intercalation into graphite is often described as due to the exfoliation of graphite whether or not exfoliation has been observed. The distinction that needs to be made is whether the flat discharge potential (voltage plateau) observed in a Li/C cell in PC-containing electrolyte at about 0.9 V vs Li/Li⁺ is due to Li⁺(PC)_n intercalation (and subsequent decomposition of the intercalate with exfoliation of the graphite) or due to the direct reduction of PC on graphite surface with exfoliation of graphite as an event occurring with some graphites.

It is reported that PC reduces on lithium, noble metals, and graphite-carbon at low potentials in the presence of Li-ions to form CH₃CH(OCO₂Li)CH₂OCO₂Li, propylene gas, CH₃CH=CH₂, and possibly Li₂CO₃ as the products.^{10,19-22} In order to shed further light on the lack of Li intercalation into graphite in PC-based electrolytes, we studied the effect of lithium, sodium, and tetrabutylammonium (TBA) cations having the same anion, namely PF₆⁻. We specifically selected spheroidal-shaped natural graphite for our studies in order to determine the role of graphite morphology on PC reduction. Furthermore, we reasoned that, because intercalation of Na⁺ and Li⁺ into graphite takes place at different potentials, the PC reduction potentials observed with these salts should tell us something about the mechanism of PC reduction. We also wanted to see what the reduction potential of PC on this graphite was, and if this particular graphite showed exfoliation after a discharge (Li intercalation) in PC-containing electrolytes. Moreover, it was reported that solution reduction products do not precipitate surface films on the electrode in the case of tetrabutylammonium perchlorate, TBAClO₄, in propylene carbonate.^{20,22} Consequently, the response of this spheroidal graphite to reduction in this electrolyte should be especially informative from a mechanistic perspective, that is, whether or not the graphite exfoliation occurs concomitant with the PC reduction.

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Experimental

Spheroidal natural graphite (PNG) was provided by Superior Graphite Inc. Chicago, IL. Battery grade PC solvent obtained from EM Industries was used without further purification. Battery grade LiPF_6 was obtained from Hashimoto Chemical Corporation. The TBAPF_6 and NaPF_6 obtained from Aldrich Chemicals were used without further purification. Graphite anodes were prepared by mixing approximately 1 g of the graphite with Kynar-2801 (PVdF-HFP), super P carbon, and *N*-methylpyrrolidone (NMP) solvent. The electrode composition was 87 wt / graphite, 10 wt / Kynar, and 3 wt / super P. The amount of NMP used to make the slurry was adjusted so that the slurry was 47 wt / solids. These materials were coated on a copper foil with a metering rod and then vacuum dried at 100°C overnight. The calendared anodes were then punched to 1.26 cm² area per side and used to construct Li/C cells.²³

Li/C cells were galvanostatically cycled in three different electrolyte solutions comprised of 1 M LiPF_6 , 1 M NaPF_6 , or 1 M TBAPF_6 in PC. The discharge tests were conducted in a standard two-electrode coin cell (model 2032, NRC Canada) with lithium counter electrode.²³ These cells were hermetically sealed inside a glove box (Vacuum Atmospheres glove box, moisture content below 1 ppm) using standard procedures. The Li/C coin cells were discharged (reduction reaction at the graphite electrode) initially at the C/20 rate (current density of 0.2 mA/cm²) in all three PC solutions. The graphite electrodes initially discharged in PC solutions for 20 h were removed from the coin cells and reassembled with our standard electrolyte consisting of 1 M LiPF_6 in a mixture of EC:diethyl carbonate (DEC):dimethyl carbonate (DMC) (EC + DEC + DMC) (1:1:1, v/v/v). In other experiments, fresh graphite electrodes were cycled in electrolyte solutions of 1 M LiPF_6 in PC + DEC (1:2, v/v), PC + DEC + DMC, (1:1:1, v/v/v), and DEC + DMC, (1:1, v/v) solvent mixtures for comparison.

Constant current (galvanostatic) tests were performed using Maccor multichannel (model 2000). All the tests were performed at a constant temperature of 20°C in an incubator (VWR, model 2005, USA).

The conductivities of the solutions were measured with a Metrohm 712 conductivity meter using Orion 018010 or Metrohm AG 9101 conductivity cells (the cell constant was $\sim 1 \text{ cm}^{-1}$). The conductivity cell was enclosed in an airtight Ace Glass-Thread glass jacket by means of Ace-Thread Teflon adapter and an FETFE O-ring. The cell contained 6–7 mL of the solution. This design of the conductivity cell allows conductivity measurements to be conducted outside the glove box without atmospheric contamination. The temperature of the conductivity cell was maintained at $\pm 0.1^\circ\text{C}$ by means of a Tenney Environmental chamber between -40 and 85°C at 10°C intervals.

The electrolyte solutions were dissolved in CDCl_3 and the ¹³C NMR experiments were conducted using the Bruker Inc. Instruments DPX-300 NMR system. All the chemical shifts are reported relative to ¹³C signal of tetramethyl silane (TMS), which was added to the sample as an internal reference to a concentration of $\sim 5\%$ (by volume).

The graphite electrodes recovered from the coin cells were washed in DEC, dried under vacuum, and characterized by means of X-ray diffraction (XRD) using a Cu K α source (Rigaku, Geigerflex), SEM (JOEL JSM-840).

Results

The spheroidal morphology of the graphite used in this study is depicted in Fig. 1. A Li/graphite cell (termed a half-cell to follow the convention used in battery literature to discuss individual electrodes) fabricated with freshly prepared graphite electrode in PC electrolyte had an open-circuit potential of ca. 3.0 V. The coin cells were discharged to 10 mV (vs Li/Li^+) at 0.2 mA/cm², and the results are presented in Fig. 2. The graphite electrode potential first drops sharply to about 1 V and then stays at a plateau voltage of ca. 0.8 V (vs Li/Li^+) in all three electrolyte solutions. Eventually, the dis-

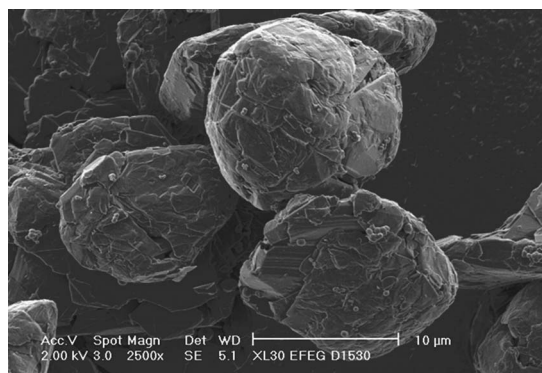


Figure 1. SEM images of pristine natural graphite powder.

charge ends with the cell potential reaching the lower cutoff voltage limit of 10 mV. These electrodes showed no capacity when charged back to 1.3 V (vs Li/Li^+), indicating that there was no Li intercalation into the graphite during the discharge.

The graphite electrodes recovered from the coin cells, after the discharges in the three electrolyte solutions as described above (see Fig. 3), were reassembled in coin cells with new separators, fresh lithium counter electrodes, and the electrolyte, $\text{LiPF}_6/\text{EC} + \text{DEC} + \text{DMC}$ (1:1:1, v/v/v). Figure 3A shows the voltage profiles of these Li/graphite cells for the initial cycles. The very high irreversible capacity, i.e., significantly less charge (Li deintercalation) than discharge (Li intercalation) in the first cycle is related to the reduction of residual PC left in the graphite electrode. We had made no attempt to remove the residual PC from the electrodes before reassembling them in new cells in order to avoid physical changes in the electrode during the reassembly process. The voltage profiles on the charge cycle and the successive discharge-charge cycles clearly show lithium intercalation as observed with fresh electrodes in the standard solution. Figure 3B displays the 15th discharge-charge cycle in the standard solution for the graphite electrodes previously cycled in PC solution and for a fresh graphite electrode. The voltage profiles of the precycled graphite electrodes clearly show the lithium intercalation staging processes, and they have comparable capacities to that of the fresh graphite electrodes cycled only in the standard electrolyte from the beginning.

Figure 4 depicts a family of XRD patterns taken from fresh (uncycled) graphite electrode, and the graphite electrodes predischarged in the three different PC solutions as indicated. There are no extra diffraction peaks, or peak shifts, for the graphite from the discharged graphite electrodes compared to the pristine electrode. The XRD

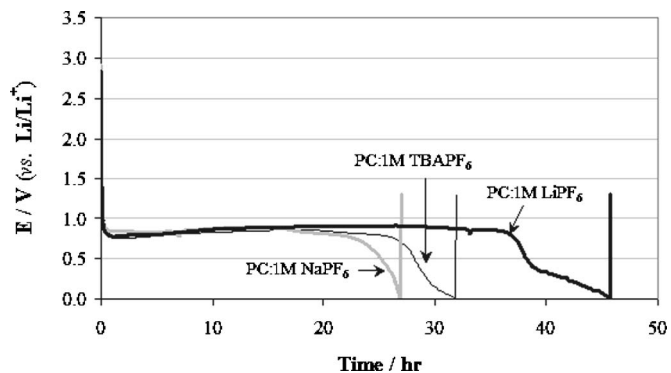


Figure 2. The voltage profiles of the Li/graphite cell in PC: 1 M LiPF_6 , PC: 1 M NaPF_6 , and PC: 1 M TBAPF_6 solutions during the first discharge (lithium intercalation) cycle. The coin cells were discharged to 10 mV (vs Li/Li^+) at 0.2 mA/cm².

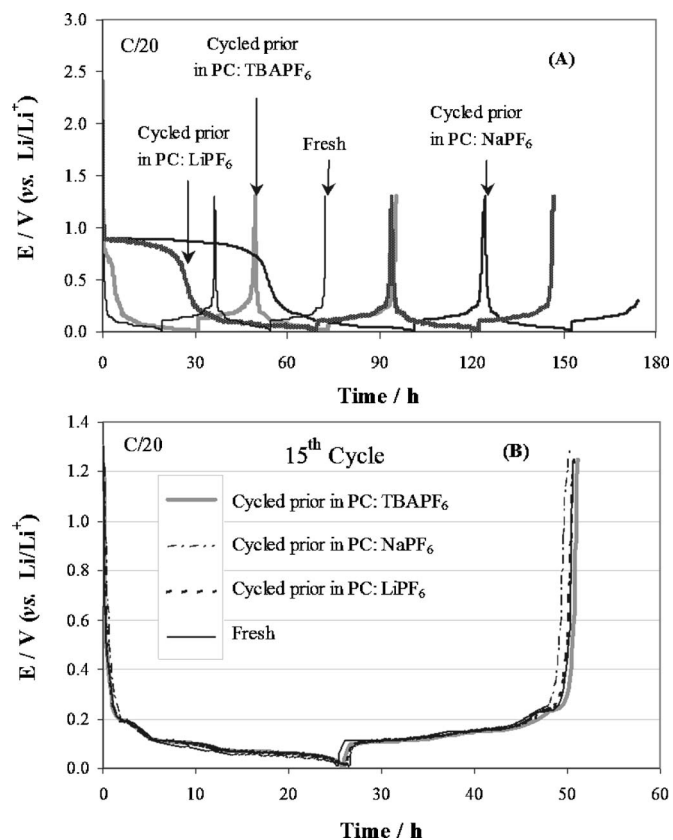


Figure 3. The voltage profile for the first two (A), and 15th (B) charge-discharge cycles obtained from graphite electrodes of fresh and once cycled in the three different PC solutions (shown in Fig. 2). The electrolyte used was 1 M LiPF₆; EC:DEC:DMC (1:1:1, v/v/v) solution. The very large irreversible plateau in (A) for the once cycled graphites was due to residual PC reduction. The graphite exhibited a specific capacity of ca. 340 mAh per gram.

patterns in Fig. 4 affirm that the graphite crystal structure is preserved even after 20 h of discharge in PC solutions.

A good understanding of the reduction mechanism of PC on graphite requires knowledge of the properties of electrolyte solutions in PC. In particular, it is useful to study the temperature dependence of conductivity as it is strongly influenced by the interactions between the solvent and the salt, usually through the formation of complexes between the two. Thus, conductivity of the electrolyte

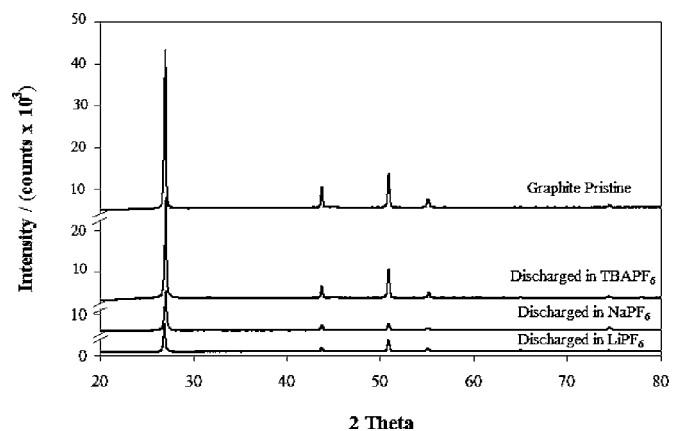


Figure 4. Comparison of XRD spectra of the graphite electrodes before and after they were discharged in PC solutions as indicated in Fig. 2.

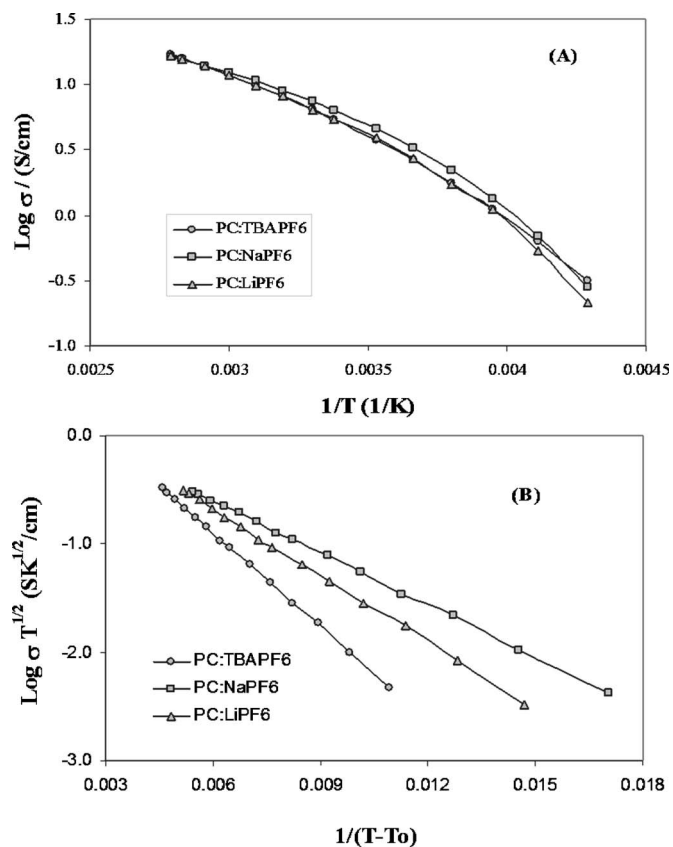


Figure 5. (A) displays the Arrhenius conductivity-temperature plots for three electrolytes. (B) shows the plots of the conductivity-temperature data in the VTF coordinates. The T_0 values labeled in the graph are obtained from fitting the data to the VTF equation (i.e., $T_0 = T_g$).

solutions is an important parameter that can provide information on ion-solvent interactions. The formation of salt-solvent complexes (solvates) can be gleaned from NMR data of the electrolytes as well.

We measured the conductivities of all three PC-based electrolyte solutions over the temperature range of -40 to $+85$ °C. The plots of conductivity vs temperature data for the PC solutions plotted in the Arrhenius coordinates are presented in Fig. 5A. The PC/TBAPF₆ and PC/LiPF₆ solutions show nearly equal conductivities above -20 °C. Although the cation TBA⁺ is much bigger in size than Na⁺ or Li⁺, the conductivities are nearly the same for all solutions. A higher degree of dissociation of TBAPF₆ resulting from the larger size of the TBA cation and weaker ion pairing have to be considered. The conductivity vs temperature profiles are characterized by a nonlinear (curved) profile, indicating that the conductivity-temperature behavior is better correlated by the VTF relationship as shown in Fig. 5B.^{24,25} The curve-fitting parameters were obtained from a nonlinear least-squares computer programming previously developed in this laboratory.²⁶ The data support the view that the ions conduct via a solvent-assisted mechanism in which the motions of the ions are facilitated by the motion of the solvent molecules. This is easily understood for the Li- and Na-containing solutions in which, as will be seen below from ¹³C NMR data, the cations are solvated by PC. Solvation of TBA⁺ by PC is not apparent as indicated by the NMR data. The conformance of the conductivity data for TBAPF₆ with the VTF behavior must then be related to electrostatic interactions between the salt ions and PC, supporting the view that the solvent and ions strongly interact in highly conductive electrolyte solutions.

The ¹³C NMR chemical shift is a powerful tool for probing the interaction between alkali metal cations and solvent molecules.²⁷ The interactions of the oxygen atoms in the carbonate solvents with

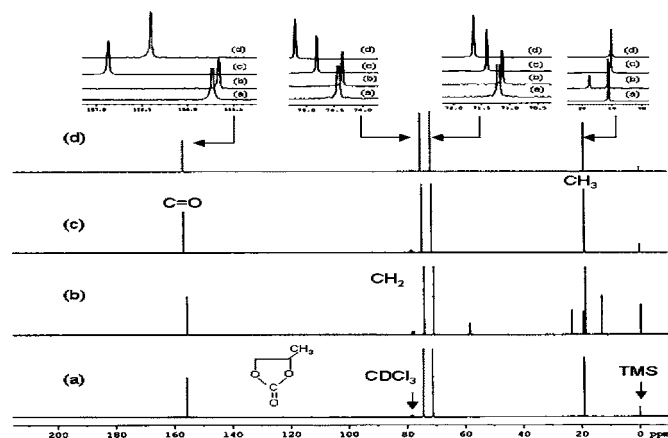
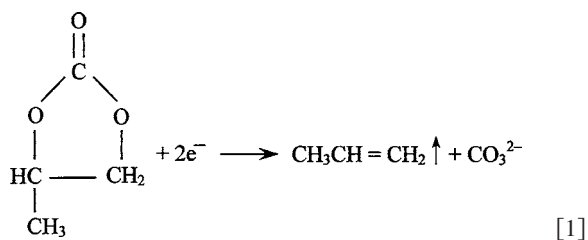


Figure 6. NMR spectra (a) PC, (b) PC: 1 M TBAPF₆, (c) PC: 1 M NaPF₆, and (d) PC: 1 M LiPF₆ solutions. Insets show expanded scale of the individual peaks.

the alkali metal cations to form solvates produce chemical shifts in the ¹³C resonance of the nearby carbons. We studied the ¹³C NMR chemical shifts of carbonyl carbons for pure PC and PC solutions with TBAPF₆, LiPF₆, and NaPF₆. Figure 6 shows the ¹³C NMR spectra of pure PC and the PC in the presence of 1 M salt as indicated in Fig. 6. The peak ca. 157 ppm corresponding to the chemical shift of the carbonyl carbon of PC shows a positive chemical shift of ca. 1.0 ppm in the case of PC:LiPF₆ and PC:NaPF₆ solutions, while the corresponding peak for PC:TBAPF₆ shows very negligible shift <0.1 ppm. The positive shifts from those of the solvents in the presence of an alkali metal salt indicate the electronic shielding of the nuclei due to electrostatic interaction between the alkali metal cation and the solvent molecules.²⁴⁻²⁶ Therefore, in the case of both LiPF₆ and NaPF₆ salts solutions, Li⁺ and Na⁺ ions are solvated (complexed) to the carbonyl oxygen atoms of PC. This agrees well with the view that the coordination between Li⁺/Na⁺ and carbonate oxygen atoms of the solvents is the thermodynamically favored reaction in the solvation process.^{28,29} There is no apparent coordination between TBA⁺ and organic carbonate oxygen atoms.

Discussion

Dey et al.¹⁰ initially proposed a two-electron process for the reduction of PC on graphite and explained the observed propylene gas formation in terms of the reaction



They observed the reduction potential at ca. 0.6 V vs Li/Li⁺, a potential not corrected for the IR drop, and did not consider an intercalation process either involving solvated or nonsolvated Li⁺ into graphite. Aurbach studied the redox behavior of PC/LiClO₄ solution on gold using steady-state cyclic voltammetry and observed that the cathodic current due to PC reduction begins at about 0.8 V vs Li/Li⁺.² Although gold can form an alloy with Li below 0.5 V vs Li/Li⁺, the process that begins at ~0.8 V is due to the reduction of PC into ROCO₂Li (R = CH₃-CH-CH₂) species, CH₃CH=CH₂ and Li₂CO₃ as major components.^{21,30} The extra methyl group of the PC reduction product is expected to interfere badly with both the cohe-

sion and adhesion of the PC reduction products, compared with the EC reduction products. The apparent closeness in the reduction potentials on gold and graphite suggests that the same process occurs on both electrodes, and that intercalation of Li⁺(solvent)_x is not necessary to explain the reduction potentials of PC on graphite. The gas evolution due to PC reduction exerts pressure on the graphite crevices; this may increase the reactive surface of the particles, and allow further surface reactions, gas accumulation inside the crevices, cracking, and an increase in the active surface area. Aurbach studied EC reduction on graphite and concluded that (CH₂OCO₂Li)₂ is formed by disproportionation of anion radical resulting from a one-electron reduction of EC. Alternatively, a two-electron reduction of EC forms CO₂ ethylene gas, or an organic polymer on the carbon surface. This scheme also suggests a possible formation of species such as LiCH₂CH₂OCO₂Li.¹⁹ Jiang et al. proposed that the secondary radical intermediate in the reduction of PC is a thermodynamically more stable species than the primary radical formed from EC, suggesting that EC reduction on graphite is less favorable than PC reduction.¹⁴ Thus, the behavior of EC is markedly different from that of PC on graphite electrode. The lithium salt also reduces at low potentials, with the result that a passivating surface film consisting of organic and inorganic reduction products formed on the graphite electrode in EC-based electrolytes. This passivation layer serves as a protective SEI for graphite because of its insolubility in EC together with the ability to selectively conduct Li⁺ ions. It prevents extensive reduction of EC and allows the cell potential to polarize to the level where Li intercalation into graphite occurs beginning at ~0.3 V vs Li⁺/Li. The formation of propylene gas from the reduction of PC has been confirmed by many following Dey's original work, including by us using IR spectroscopy.²⁶ It appears that in PC the initial one-electron reduction product (for example, CH₃CHCH₂OCO₂Li) is soluble in the electrolyte and continues to be reduced to form Li₂CO₃ and propylene gas. The result is a lack of protection for the graphite electrode from an SEI and extensive reduction of PC. The Li/C cell voltage remains at about 0.8 V until a substantial amount of PC is reduced. The SEM data shown in Fig. 7 suggest that a film is formed on the graphite electrode concomitant with PC reduction, most probably ROCO₂Li species; propylene gas and Li₂CO₃ do not appear to have the properties of an SEI.

The ¹³C NMR chemical shift data presented in Fig. 6 clearly show that Li⁺ and Na⁺ ions in the LiPF₆ and NaPF₆ solutions, respectively, are solvated by PC. The NMR data, do not show evidence for strong interactions between the TBA cations and PC. In all three solutions the first discharge of the Li/graphite cell takes place at practically the same potentials. It is generally believed by most, despite occasional reports to the contrary, that the relatively flat discharge potential observed at ~0.8 V for the first discharge of Li/graphite cells with PC/Li salt solutions corresponds to the co-intercalation of Li(PC)_n⁺ into the graphite lattice followed by the reduction of PC and exfoliation of the graphite. Our results show that the spheroidal graphite electrodes we have cycled in PC solutions did not intercalate lithium. Instead, the graphite electrodes retrieved from these Li/C cells, after extensive PC reduction, and reassembled and tested with standard Li-ion battery electrolyte, exhibited as depicted in Fig. 2 reversible Li intercalation capacities and voltages identical to those exhibited by fresh graphite electrodes. It is clear from these results that the reduction process observed at about 0.8 V most probably involves the reduction of PC on the graphite surface as found on metal electrodes. This is not to discredit exfoliation of highly ordered graphite anodes such as the highly oriented pyrolytic graphite (HOPG) reported by others in PC-based electrolytes. The edge planes of graphite are preferred sites for reduction of organic compounds and some penetration of the reduction reaction into the graphite layers is possible.¹⁸ In those cases where the reduction involves a gaseous product, exfoliation of graphite can occur with many forms of graphite due to the pressure of the gases, primarily propylene, produced at the edge faces of the graphite particles where solvent reduction reaction is more catalytic than on the basal planes.

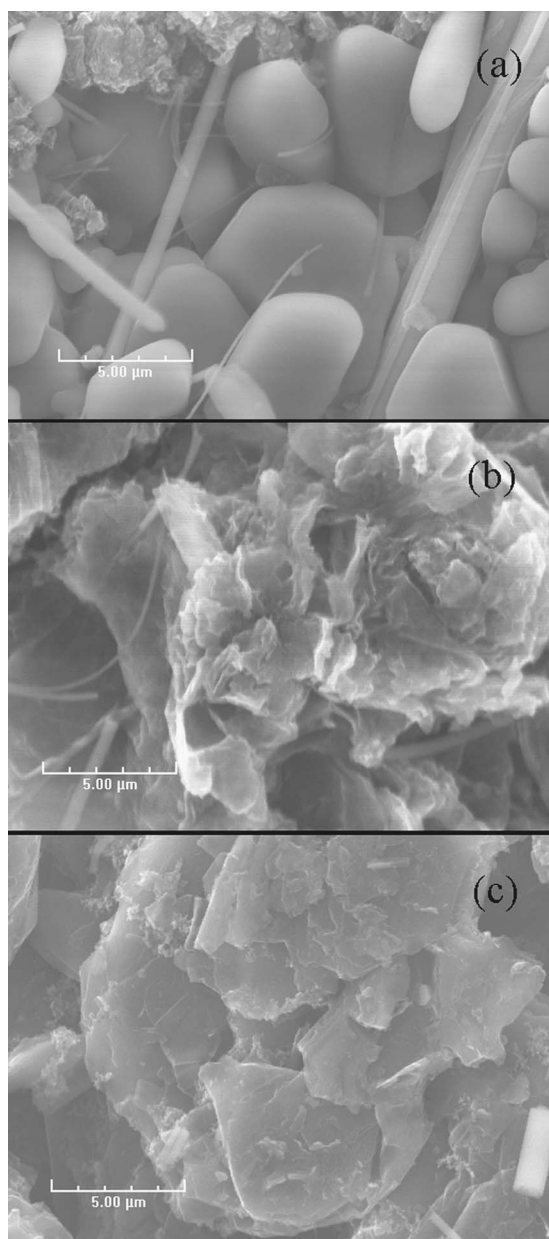


Figure 7. SEM images of graphite surface discharged (lithium intercalation) in (a) PC: 1 M TBAPF₆, (b) PC: 1 M NaPF₆, and (c) PC: 1 M LiPF₆ solutions.

There have been many studies to elucidate the mechanism of the reduction of PC on carbon electrodes in Li-ion conducting electrolytes, although most of these studies utilized HOPG. In most cases the reduction of PC at 0.8–0.9 V is accompanied by swelling and apparent exfoliation of the graphite. XRD studies of the graphite electrode in a Li/C cell with PC-based electrolyte performed at various stages along the 0.9 V reduction potential plateau showed no evidence of graphite exfoliation.¹⁴

The question that needs to be asked is, is PC cointercalation an a priori step in the reduction of PC on the graphite electrodes we used? Do we see differences in the reduction potentials of PC if we use a graphite electrode in which PC cointercalation is not possible due to structural reasons such as a spheroidal morphology? Do we see differences in the reduction potentials of PC when the supporting electrolyte is NaPF₆, in which the Na ions are solvated with PC, or when the supporting electrolyte is TBAPF₆, in which there is little apparent solvation of the TBAP cation by PC? The data pre-

sented earlier clearly indicate that the reduction potential of PC on the spheroidal graphite electrode in the various electrolytes is virtually the same as that observed previously on other graphite electrodes, including the much-studied HOPG. Furthermore, there are no differences in the PC reduction potentials attributable to the nature of the salt used (Fig. 2). In all these solutions and on graphite electrodes PC is reduced at practically the same potentials as that on metal electrodes. The scanning electron microscope (SEM) micrographs of Fig. 7 depict the surfaces of the graphite electrodes retrieved from the NaPF₆ and LiPF₆ containing cells after the discharge experiments of Fig. 2. The graphite surfaces are covered with a precipitate of the reduction products, most probably ROCO₂Li species or Li₂CO₃. The electrode from the TBAP cell is only partially covered by a reduction product, in agreement with a previous study that indicated that a protective surface film is not formed on the electrode during reduction of PC/TBAClO₄ solution.³¹ The presence of an endpoint in the discharges of the various cells in Fig. 2 may be due to the electrode surface being passivated by some reaction products while PC is being depleted by the reduction decomposition process, although the reaction products do not have protective SEI properties. Noticeably, the graphite particles show little evidence for exfoliation despite substantial PC reduction on it. The X-ray data in Fig. 4 strongly support this view. The graphite electrodes retrieved from the cells perform as well as the new graphite electrode when reassembled and cycled with the standard Li-ion battery electrolyte. It is clear from the results presented here that cointercalation of PC and Li⁺ most probably does not occur, at least in these graphite electrodes. Exfoliation of some graphite may occur if there is opportunity for the reduction reaction process to penetrate into the graphene layers.

The spheroidal graphite electrodes used in this study enabled us to investigate the manner in which different carbonate solvents influence the Li intercalation process without interference from solvent cointercalation. The DEC/LiPF₆ electrolyte showed little ability to intercalate Li into graphite (Fig. 8b) as evidenced by the fact that it was not possible to recharge the electrode after the first discharge. The process apparently involved only the reduction of DEC despite the fact that the potentials were substantially lower than those observed with PC. In a DMC-based electrolyte, appreciable Li intercalation occurred, as evidenced by the good rechargeability for the discharge capacity in the first discharge. These data are presented in Fig. 8a, where the performance of Li/C cells with DEC and DMC-based electrolytes is compared to that with the standard Li-ion battery electrolyte.

A PC/DEC mixed electrolyte shows behavior very similar to the cells tested with neat PC or DEC electrolytes, while a cell with the mixed electrolyte prepared from PC, DEC, and DMC performs similar to the cell containing DMC. The first cycle results for these cells presented as differential capacities in Fig. 9 clearly show the potentials at which the various solvents reduce on the electrode and their influence on the electrode's ability to intercalate Li and afford rechargeability. EC reduction occurs with good passivation protection of the graphite electrode, and Li intercalation is highly reversible. DMC reduces at a slightly higher potential than PC with good protection of the graphite electrode by its reduction products, and reversible Li intercalation is possible in a DMC/LiPF₆ solution. PC reduces at about 0.8 V vs Li⁺/Li with little protection of the graphite electrode, and DEC reduces below 0.8 V without forming a protective SEI as well. In both PC and DEC solutions Li intercalation is difficult to achieve unless an SEI-forming solvent such as EC or DMC is present. In all these cases there is little evidence for solvent cointercalation along with Li.

Conclusions

Lithium intercalation into graphite possessing a spheroidal particle morphology was investigated in PC-based electrolytes containing LiPF₆, NaPF₆, or (C₄H₁₀)₄NPF₆ as the supporting electrolyte. The data from Li/C cells utilizing these electrolytes showed that reduction of PC occurs on the graphite electrode at about 0.8 V vs

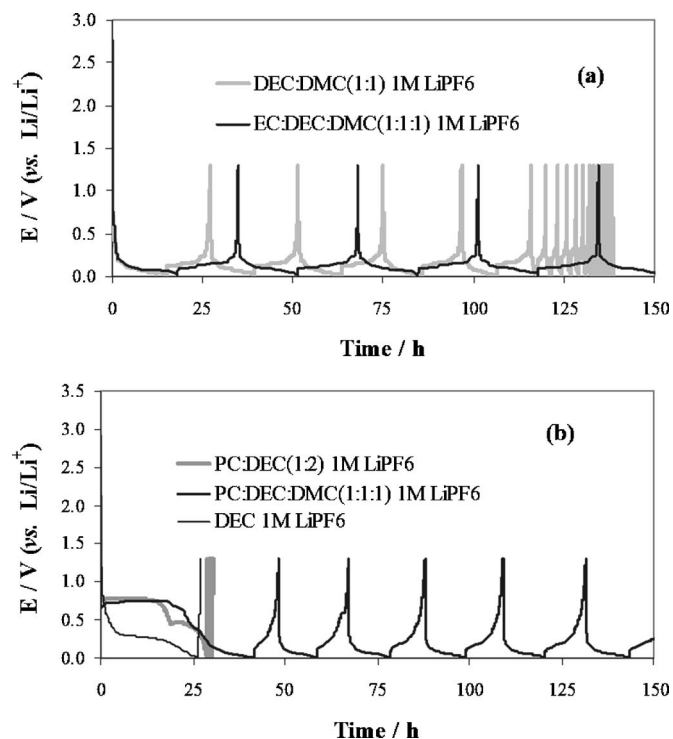


Figure 8. The voltage profile for the first few cycles of charge-discharge cycles obtained from fresh graphite electrodes. The electrolytes used were (a) 1 M LiPF₆: DEC + DMC (1:1, v/v), 1 M LiPF₆: EC + DEC + DMC (1:1:1, v/v/v), and (b) 1 M LiPF₆: PC + DEC (1:2, v/v), 1 M LiPF₆: PC + DEC + DMC (1:1:1, v/v), and 1 M LiPF₆: DEC solutions. Cycled at a current density of 0.2 mA/cm².

Li⁺/Li with little Li intercalation. The PC reduction potentials showed no dependence on the supporting electrolyte salt present in the electrolyte. Furthermore, there was no evidence for PC cointercalation into the graphite lattice as Li⁺(PC)_n, nor was any exfoliation of the graphite used. The potentials at which PC is reduced are very similar to those previously identified with graphite electrodes, in which PC and Li⁺ cointercalation apparently occurred at about the same potentials as found in this study. Our data suggest that cointercalation of PC is most probably not responsible for the observed potential profiles of graphite electrode we used, but it is due to the simple reduction of the solvent on the graphite electrode surface. It is our view based on our results that any graphite exfoliation observed in prior studies was opportunistic in nature coming from the unique morphology of the graphite electrode as in the case of the HOPG. EC and DMC are reduced on graphite at slightly higher potentials than PC is, and their reduction products serve as SEI on the graphite surface protecting it from extensive solvent reduction. This promotes reversible Li intercalation in these solvents and their mixtures. DEC-based electrolytes behave similar to PC although the reduction of DEC occurs at lower potentials than PC. Although PC and DEC are not useful for use as single solvents for Li-ion battery electrolytes, they can be used as cosolvents with DMC and EC to prepare Li-ion battery electrolytes. The data presented here are useful to design and optimize electrolytes for tailoring the performance of Li-ion batteries.

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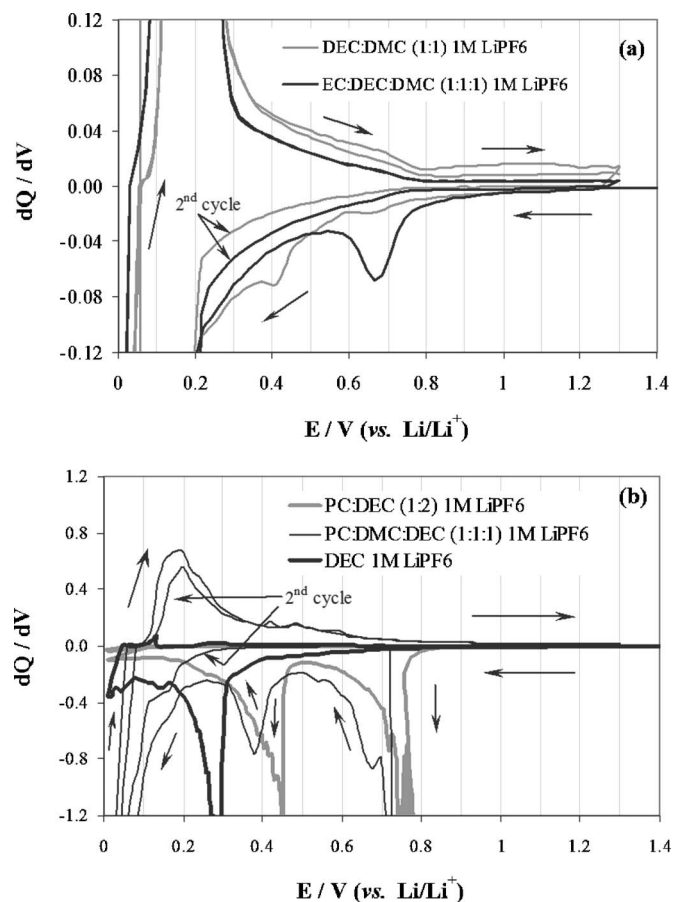


Figure 9. Differential capacity (dQ/dV) vs. potential calculated for the first two cycles shown in Fig. 8.

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