Electrochemical and spectroscopic studies of carbon electrodes in lithium battery electrolyte systems

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Abstract

In this work we studied several parameters that influence the intercalation of lithium ions into carbons (e.g. carbon type, binder and solution composition). The carbons investigated included carbon blacks (e.g. acetylene black, Ketjen black), graphite and carbon fibers. The solvents used in this study include methyl formate, propylene and ethylene carbonate, ethers (e.g. tetrahydrofuran) and their mixtures. The salts included $LiClO_4$, $LiAsF_6$ and $LiBF_4$. CO_2 was tested as an additive. The electrochemical behavior of the electrodes in solutions was followed by chronopotentiometry in galvanostatic charge/discharge cycling and their surface chemistry in solutions was investigated using surface sensitive Fourier-transform infrared spectroscopy (FT–IR) in transmittance, attenuated total reflectance and diffuse reflectance modes. It was found that the solvents and salts are reduced on the carbon electrodes at low potentials to form surface films. In general, their surface chemistry is quite similar to that of lithium or noble metal electrodes at low potential (in the same solutions). The electrochemical behavior of the carbon electrodes in terms of degree of intercalation and its reversibility is strongly affected by their surface chemistry. Reversible intercalation was obtained with graphite in methyl formate solutions containing CO_2. Some degree of reversible intercalation was also obtained with graphite in ethers. The presence of propylene carbonate in solution is detrimental for lithium intercalation in graphite. Reversible lithium–carbon intercalation was also obtained with acetylene black and carbonized polyacrylonitrile. The binder types have a strong impact on the electrode's performance. Preliminary guidelines for optimizing the performance of carbon electrodes as anodes in rechargeable lithium battery systems are discussed.

Introduction

Safety and cycle-life problems related to the lithium metal anodes in ambient temperature secondary Li batteries have led to an intensive search for alternative anodes for high-energy rechargeable Li batteries.

The class of alternative anodes for Li batteries, on which most attention has been focused recently, is Li–C intercalating compound (at the theoretical stoichiometry of LiC_6) [1–3]. A reversible intercalation of Li has been observed with several types of

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carbon electrodes, including graphite [4], carbon fibers [5], and petroleum coke [1], in Li salt solutions of polar aprotic solvents (e.g., propylene carbonate (PC), ethylene carbonate (EC) [1–5], ethers, dimethyl sulfoxide (DMSO) [6]).

Recently, there were also reports about prototypes of rechargeable batteries in which Li–C intercalation compounds are the anode materials, metal oxides are the cathode materials and the electrolytes are Li salts in polar aprotic solvents [7]. Metal oxides such as CoO_2, NiO_2 Mn_2O_4 reversibly intercalate with Li at potentials around 4 V in the Li/Li^+ scale [8, 9]. By choosing the proper carbon as the anode and metal oxide as the cathode, working voltages of 3 to 4 V can be obtained. Thus, the batteries still maintain quite a high energy density despite the fact that the light Li anode is replaced by LiC_6 compounds.

When carbon electrodes are cathodically polarized in Li salt solutions of polar aprotic solvents, the first process is partly irreversible and may involve much more charge transfer than is expected from the stoichiometry of the Li–C intercalation reaction (LiC_6). This extra charge may be related to an irreversible reduction of solution components [1–3].

It is known that Li surfaces in polar aprotic solvents are covered with films formed by precipitation of species which are the reaction products between Li and solution components (e.g., solvents, salts and contaminants). These surface films control the electrochemical behavior of Li in solutions [10]. Li–C intercalation occurs at potentials higher than the Li rest potential. Therefore, one would expect lithiated carbon to be less reactive than Li metal with solution components. In fact, this assumption led to lithiated carbon electrodes being considered as alternative anodes for Li batteries. However, in previous work, we found that many polar aprotic solvents including PC, EC, ethers (e.g., THF), butyrolactone (BL) are reduced at potentials much higher than Li rest potential [11–13]. Lithium salts such as $LiAsF_6$ or $LiClO_4$ are also reduced at potentials between 1 to 1.5 V versus Li/Li^+ [14]. We found that nonactive metal electrodes, (e.g., Pt, Au, Ni) treated in Li salt solutions of solvents such as PC, EC, methyl formate (MF) or ethers at potentials below 1 V (Li/Li^+) are covered with surface species quite similar to those formed on Li in the same solutions [11–15]. Therefore, the electrochemical behavior of lithiated carbon electrodes in the various electrolyte solutions may be controlled by a surface chemistry similar to that of Li in the same systems.

This work involves the study of the lithiation process of several types of carbon electrodes including graphite, carbon blacks and carbon fibers in a variety of key electrolyte solutions. The solvent includes alkyl carbonates (PC and EC), ethers (tetrahydrofuran (THF), dimethoxyethane (DME) and 1,3-dioxolane) and MF.

The effect of CO_2 as an additive was also studied because it was found that the presence of CO_2 increases Li cycling efficiency in MF solutions [8].

The influence of the binder used in the carbon electrodes (e.g., Teflon, ethylene/propylene/diene polymer (EPDM), polyvinylidene difluoride (PVDF)) on their performance was also explored.

The electrochemical behavior of the various systems was studied by chronopotentiometry and the surface chemistry of the carbon electrodes was studied by surface sensitive Fourier–transform infrared spectroscopy (FT–IR) in transmittance, attenuated total reflectance (ATR), and diffuse reflectance modes.

The theme of this work is the study of a large matrix of parameters (e.g., type of carbon, binder, solvent, salt and additives) in order to determine the important factors that influence Li–C intercalation.

Experimental

The following carbons were used: Ketjen black: KB (700 m^2/gr, EC-300, AKZO), Antralur: Ant. (1200 m^2/gr, KC: Lurgi), acetylene black: AB (70 m^2/gr, Gulf), synthetic graphite: GR (9 m^2/gr, KS-44, Lonza), and carbonized polyacrylonitrile: PAN (Grafil). Three types of binders were used, EPDM, polytetrafluoroethylene (Teflon PTFE) and PVDF.

The carbon electrodes were prepared by a wet mixing of carbon materials, binder (4–5 wt.%) and a solvent (H_2O in the case of PTFE and PVDF and cyclohexane in the case of EPDM). This mixture was rolled onto a stainless-steel screen, dried and sintered. The electrodes thus formed were 0.3 to 0.5 mm thick. Prior to the measurements, all electrodes were vacuum dried for a few hours by heating in a vacuum oven.

Preparation for the electrochemical and spectral studies were done under high purity argon atmosphere in glove boxes using high purity solvent and salts [11–15].

The carbon electrodes were studied in glass cells in a parallel plates configuration using Li foil counter electrodes and polyethylene spacers. Their electrochemical behavior was studied in galvanostatic charge/discharge cycling, using the Series 2000 Maccor computerized multichannel battery charger. In order to carry out measurements in parallel, the cells containing the electrodes were stored in sealed aluminum pressure vessels and measured out of the glove boxes. When needed, these vessels could be pressurized with CO_2 up to 15 atm.

Due to problems of mechanical stability of the electrodes, the accuracy and reproducibility of the measurements (e.g., the charge involved in each process) is estimated as $\pm 4\%$.

FT–IR spectroscopy (Nicolet 60 SXB spectrometer) of electrodes was conducted using three models of operation: (i) transmittance — the carbon particles were pelletized with KBr; (ii) attenuated total reflectance (ATR) — the carbon electrodes were pressed onto ZnSe prism and the multiple internal reflectance was measured using Harrick ATR attachment [16], and (iii) diffuse reflectance — the carbon particles were scraped from the electrodes and measured directly when placed in the appropriate accessory (Harrick DRIFT attachment).

The electrodes were measured *ex situ* before and after the electrochemical processes after being washed in pure solvent and vacuum dried.

Results and discussion

The influence of the carbon and the electrolyte systems on Li–C intercalation

Figure 1 presents the charge/discharge behavior of four types of carbon electrodes in 1 M $LiAsF_6$ solution in MF under CO_2 atmosphere (3 atm). The voltage was measured against the Li counter electrodes in galvanostatic experiments with a charging voltage limit of 0 to 0.1 V and a discharge limit of 1.5 to 2 V.

The charges involved in the various processes are also marked in Fig. 1 and are expressed in equivalents per 6 moles of carbon (x in Li_xC_6), where $x = 1$ corresponds to a fully lithiated carbon (a charge of ≈ 372 mA h per g of carbon).

As shown in Fig. 1, each carbon behaves differently. The first charging process, which should lithiate the carbon, requires much more charge than that needed for a full lithiation of the carbon.

There is no simple correlation between the surface area of the carbons and the charge involved in the first process. However, more charge is involved in the first
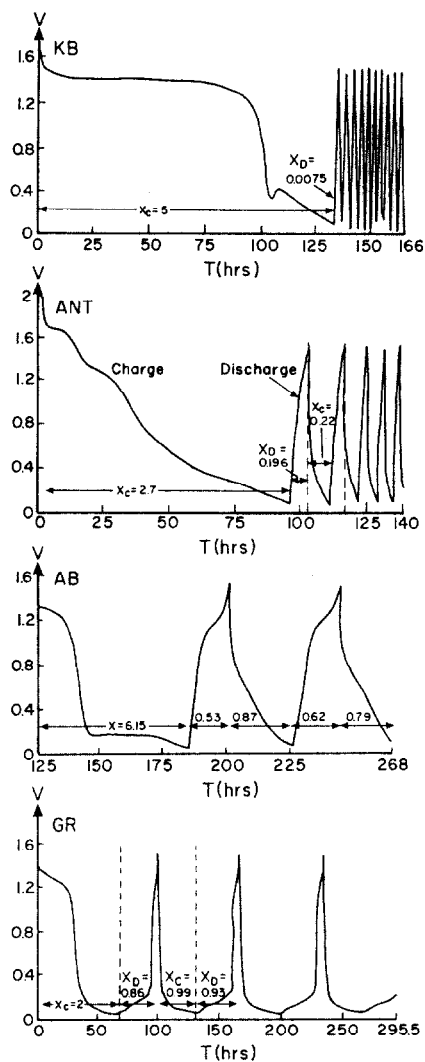
Fig. 1. The voltage–time behavior of various carbon electrodes in galvanostatically charge/discharge cycling in MF–1 M LiAsF$_6$ solution under CO$_2$ pressure (3 atm). The carbon electrodes were treated in cells containing Li counter electrodes and the voltage recorded is therefore vs. the Li electrode. The current is reversed when the potential drops to 0.05 V (end of charge) or when it reaches 1.5 V (end of discharge). The electric charge involved in each process is expressed in equivalent per 6 moles of carbon.

cycle of the high surface area carbon blacks as compared with the low surface area graphite. Based on previous studies [11–15] related to the electrochemical windows of the various electrolyte systems used, it is obvious that all the anodic processes occurring between 0 and 2 V (Li/Li$^+$) should be related only to Li deintercalation as both the solvents and the surface species formed at low potentials are not oxidized

within this potential range. Hence, the degree of intercalation and its reversibility are indicated by the charge involved in the discharge (anodic) processes.

As shown in Fig. 1, Li ions intercalate with graphite reversibly and the degree of intercalation (x) is close to 1. Some degree of reversible intercalation also occurs with acetylene black, AB. The degree of Li intercalation with the other carbon blacks (Antralur and Ketjen black) is very low.

Figure 2 shows the behavior of PAN fibers in PC–1 M LiAsF$_6$ solutions. The voltage–time behavior of this system indicates that Li intercalates reversibly with these carbon fibers, although the degree of intercalation is only $x = 0.32$.

Table 1 summarizes the electrochemical behavior of the different carbon materials in two solvent systems (PC and MF/CO$_2$ using LiAsF$_6$ as an electrolyte). The electric capacities of the first two charge/discharge cycles are listed for each electrode, expressed as x in Li$_x$C$_6$.

The data presented in Table 1 is very significant since the charge in the first cathodic process is related to the reduction of solution species on the carbon surfaces occurring in addition to Li–C intercalation, and in cases where reversible Li–C intercalation is obtained, steady, reproducible behavior is obtained in the second charge/ discharge cycle. Hence, the numbers in the first column (first charge) represent the degree of solution reduction occurring in addition to the Li–C reaction, while the numbers in the fourth column (second discharge) represent the true degree of intercalation. The data listed in Table 1 also indicate that for the same carbon, the degree of intercalation strongly depends on the solvent system used.

Figure 3 shows typical voltage–time curves obtained in galvanostatic charge/discharge cycling of AB-Teflon electrodes in PC, THF and MF/CO$_2$ solutions of 1 M LiAsF$_6$. It seems that, to some extent, a reversible Li ions intercalation was obtained in the three solvent systems. However, each system behaves differently in terms of the charge involved in the first charging process, the degree of Li intercalation and the shapes of the voltage–time curves. The charge involved in the first process when MF is the
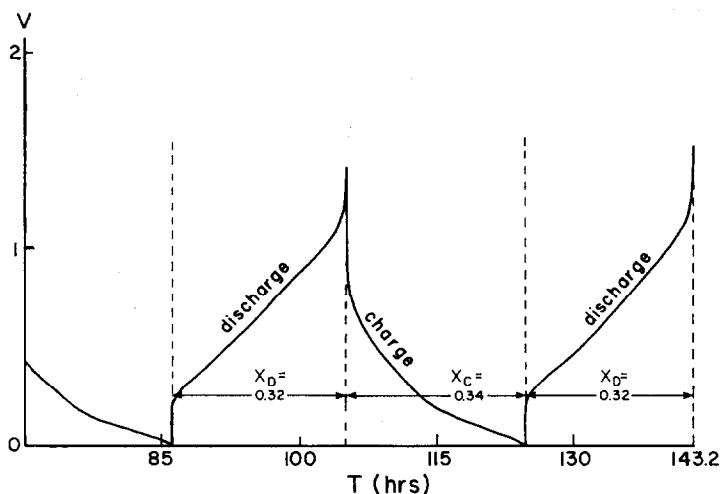

Fig. 2. Typical behavior of carbonized polyacrylonitrile–carbon fibers in PC–LiAsF$_6$ solutions (similar behavior was observed in THF). The voltage of cells containing Li counter electrode, which was charged/discharged galvanostatically, is recorded as a function of time. The current is reversed when the potential reaches the predetermined limits (0.1 and 1.5 V). The electric charge involved in each process is expressed in equivalent per 6 moles of carbon.

TABLE 1

The influence of the carbon used (binder: Teflon)[a]

Carbon	First charge	First discharge	Second charge	Second discharge
(a) PC–LiAsF$_6$ based solution				
AB	$x^b = 1.03$	0.15	0.1	0.1
KB	$x = 1.33$	0.002	0.001	0.001
Ant	$x = 0.75$	0.01	0.02	0.01
GR	$x = 0.4$	0	0	0
PAN	$x = 0.6$	0.47	0.35	0.35
(b) MF-LiAsF$_6$ solutions, CO$_2$ atmosphere (3 atm)				
AB	$x^b = 6.15$	0.53	0.87	0.62
KB	$x = 5$	0.01	0.01	0.01
Ant	$x = 2.70$	0.195	0.22	0.1
GR	$x = 2.1$	0.9	0.97	0.93
PAN	$x = 1.76$	≈ 1	≈ 1	≈ 1

[a]The charges in the first four processes (two charge/discharge cycles) are listed, expressed in equivalent per 6 moles of carbon ($x = 1$ corresponds to 372 mA h per 1 g of carbon). Average charge/discharge rate is $C/35$ h, and reproducibility of the data is estimated as $\pm 4\%$.
[b]x in Li$_x$C$_6$.

solvent which is six times more than that required for a full intercalation ($x = 1$), seems to reflect the high reactivity of this solvent compared with PC and THF [14] (where the charge involved in the first process in only 2.5 to 3.5 times the charge required for LiC$_6$ formation). The possibility of obtaining a reversible intercalation with both AB and graphite in MF solutions depends primarily on the presence of CO$_2$ as an additive.

In the case of graphite, Li–C intercalation occurs in MF–LiAsF$_6$ or LiClO$_4$ solutions, but its degree and reversibility remarkably improve when CO$_2$ is present. Figure 4 plots the electric charge (expressed in equivalent per 6 moles of carbon) involved in charge and discharge processes of graphite–Teflon electrodes in MF–1 M LiAsF$_6$ solutions as a function of the number of cycles and the CO$_2$ pressure and it shows clearly that the degree of intercalation and its reversibility increases and the charge involved in the first charging processes decrease as the pressure of CO$_2$ increases. Hence, the presence of CO$_2$ in solutions decreases the solution reactions which accompany the initial intercalation process. As will be shown in the next section, this should be attributed to the passivating properties of the CO$_2$ reaction products which precipitate on the carbon surface. This passivation, which is expressed by the decrease of the charge required for the first interaction process (Fig. 4), probably prevents the interference of the solvent interactions, which are detrimental to the stability of the intercalation compounds and to their reversible formation. In contrast, the presence of PC in solutions, either as a major solvent or as a cosolvent, detrimentally affects Li–C intercalation in the graphite we used. This is demonstrated in Fig. 5 which shows the
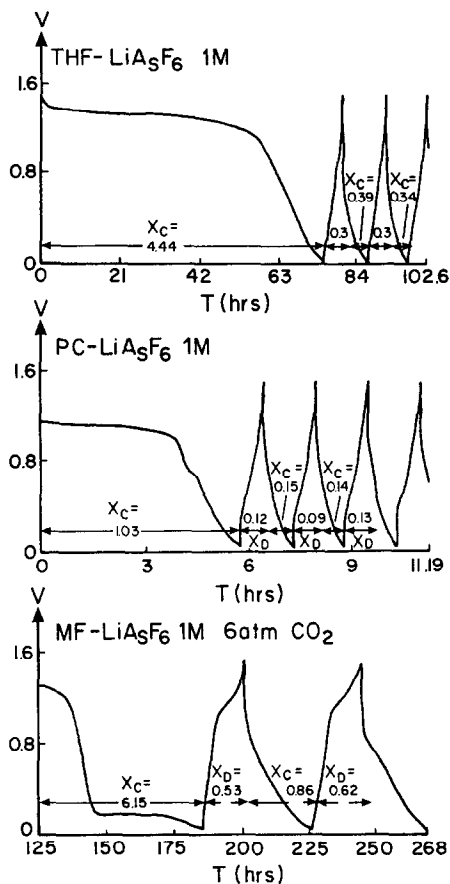
Fig. 3. The typical behavior of acetylene black–Teflon electrodes in THF, PC and MF/CO$_2$ solutions containing 1 M LiAsF$_6$. The voltage is recorded vs. Li counter electrodes in galvanostatic charge/discharge cycling. The current is reversed when the potential reaches the predetermined limits (0.1 and 1.5 V).

behavior of graphite electrodes cycled galvanostatically in MF solutions containing PC. The behavior in PC/CO$_2$ and MF/CO$_2$ is also shown for comparison.

There are other reports in the literature describing the negative effect of PC on Li intercalation with graphite, which are attributed to a destruction of the graphite structure (exfoliation) due to the interaction with this solvent (e.g., cointercalation of PC molecules and Li$^+$ in the graphite) [1]. In a few experiments 12-crown-4 was added to PC solutions in an amount equimolar to the Li salt (LiAsF$_6$). With these solutions it was possible to obtain Li intercalation with graphite. The degree of intercalation and its reversibility was poor in comparison with that obtained in MF/CO$_2$, but compared with regular PC solutions the change due to the crown ether addition was remarkable.

These results seem to prove that cointercalation of PC in graphite may be one of the reasons for its detrimental effect.
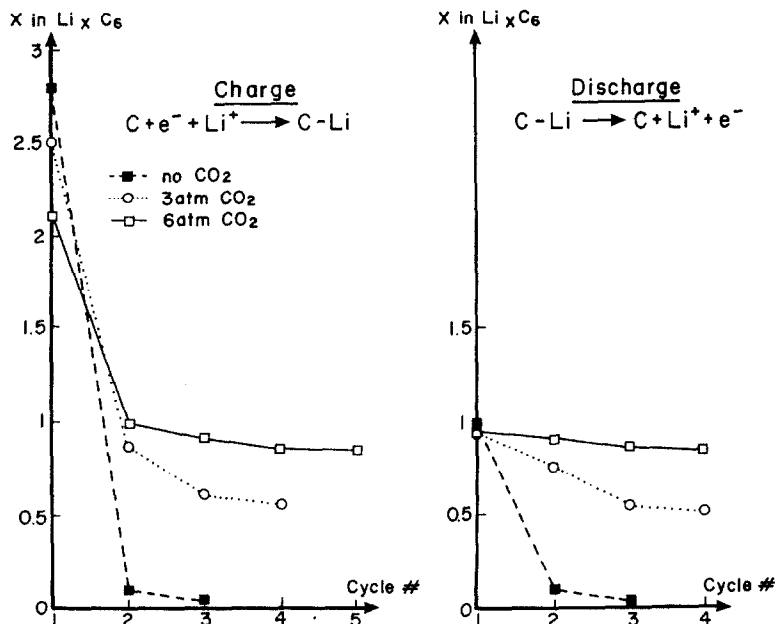
Fig. 4. The influence of the charge (expressed as x in Li_xC_6) involved in the first four intercalation-deintercalation cycles of Li–graphite electrodes in MF–1 M $LiAsF_6$ solutions, as a function of cycle number at two CO_2 pressures.

Hence, when the Li cation is solvated by the crown ether, much less solvent molecules are carried with it into the graphite intercalation sites and therefore Li–C intercalation is less disturbed.

Table 2 summarizes the electric charges involved in the first four processes (two charge/discharge cycles) of graphite and AB in the solvent systems studied. As demonstrated in the Table, the degree of intercalation and its reversibility is strongly affected by the electrolyte system used. The charge in the first cycle probably reflects both the reactivity of the solvent system used and the passivating properties of the surface species formed. It is clear from Figs. 1–5 and Tables 1 and 2 that the processes occurring in the first charging from surface species that passivate the electrodes considerably affect the intercalation reaction. The use of $LiClO_4$ instead of $LiAsF_6$ in these solvents does not strongly affect the degree of intercalation and its reversibility, but decreases the charge involved in the first process. Tentatively, one would attribute it to the better passivating properties of $LiClO_4$ reduction products as compared with $LiAsF_6$ reduction products.

Hence, the surface chemistry of the carbon in solutions plays an important role in its intercalation reaction with Li. Therefore, a special effort has been made to explore the surface species formed on carbon in the various solvent systems studied.

The surface chemistry of carbon electrodes in the various electrolyte systems studied

The basic surface chemistry of the Li and non active metals (e.g., Au, Pt and Ni) at low potentials in all the solvent systems studied was explored and characterized in previous work [11–16] and is described in Schemes 1 and 2.
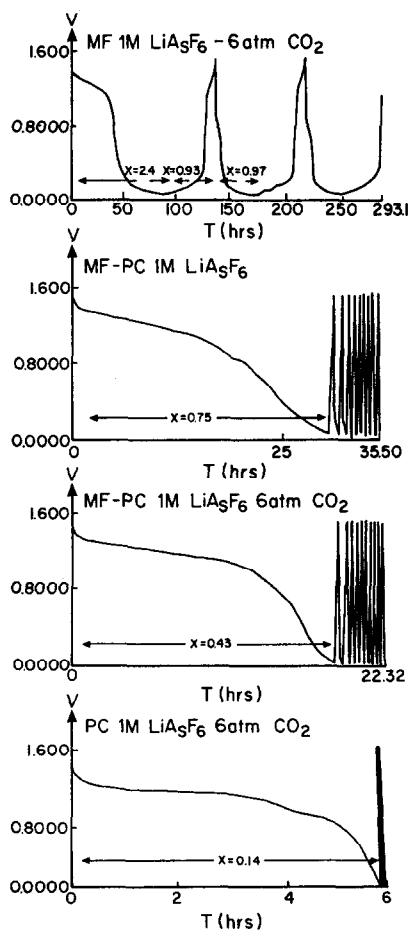
Fig. 5. The typical voltage–time behavior of graphite electrodes in galvanostatic charge/discharge cycling in MF/CO_2, MF–PC, PC/CO_2 and MF–PC/CO_2 solutions containing 1 M LiAsF$_6$. The voltage is recorded vs. Li counter electrodes and the charge in each process is expressed in equivalent per 6 moles of carbon (x in Li$_x$C$_6$).

Methyl formate

Figure 6 shows typical FT–IR spectra obtained *ex situ* from AB–EPDM and AB–Teflon electrodes polarized in MF–1 M LiAsF$_6$ solutions to 0.1 V (Li/Li$^+$) (transmittance mode). Spectrum 6(a) relates to AB–EPDM, and is typical of Li formate. This proves that MF is reduced on carbon at low potentials similarly to Li, as outlined in Scheme 1 [14]. Spectrum 6(b) relates to AB–Teflon, and is much more complicated and also has νC=O, νC−O and δ-O−CO$_2^-$ peaks (indicated in the Fig.) in addition to Li formate peaks and which are typical of ROCO$_2$Li compounds [15]. ROCO$_2$Li compounds could be formed by reaction of ROLi species formed by MF reduction to Li methoxide (see Scheme 1 and Fig. 6(b), with trace CO$_2$ during sample preparation [15].

Hence, the change of the binder from EPDM to Teflon changed the reduction path of MF on the carbon surface to form alkoxy species (probably LiOCH$_3$) in

TABLE 2

The influence of the solvent used[a]

Solvent	First charge	First discharge	Second charge	Second discharge
(a) Graphite–Teflon				
PC–LiAsF$_6$[b]	$x^c = 0.4$	0	0	0
THF-LiAsF$_6$	$x = 0.5$	0.27	0.38	0.26
DN-LiAsF$_6$	$x = 0.42$	0.37	0.014	0.013
MF-LiAsF$_6$	$x = 2.8$	0.92	0.82	0.5
MF-LiAsF$_6$/CO$_2$ (6 atm)	$x = 2.1$	0.93	0.97	0.9
(b) AB–Teflon				
PC–LiAsF$_6$[b]	$x^c = 1.03$	0.12	0.15	0.09
THF–LiAsF$_6$	$x = 4.44$	0.32	0.39	0.29
MF–LiAsF$_6$	$x = 4.8$	0.002	0	0
MF–LiAsF$_6$/CO$_2$	$x = 4.9$	0.67	0.95	0.65

[a]The charges in the first four processes (charge/discharge cycles) are listed, expressed in equivalent per 6 moles of carbon ($x = 1$ corresponds to 372 mA h per 1 g of carbon). Reproducibility of the data is estimated as $\pm 4\%$.
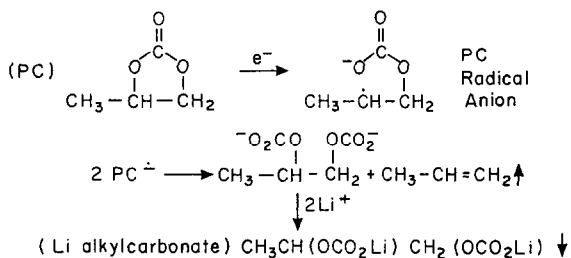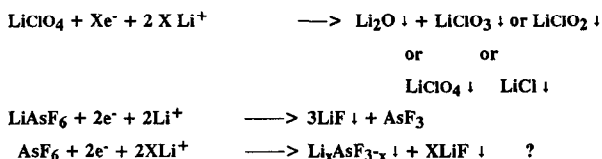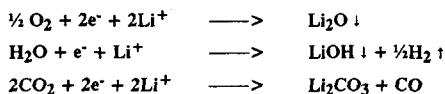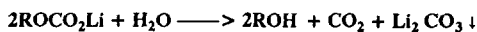[b]The LiAsF$_6$ concentration in all the solutions was 1 M.
[c]x in Li$_x$C$_6$.
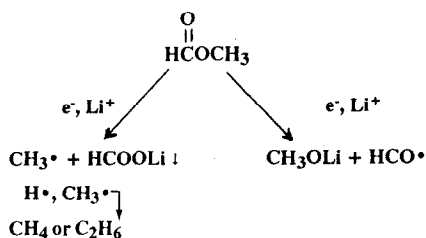
Scheme 1. Surface chemistry of lithium electrodes and nonactive electrodes at low potentials in solutions of methyl formate.

addition to Li formate. The MF reduction path depends on which of the oxygen–carbon bonds of the ester is cleaved and may be affected strongly by the nature of the surface. As will be shown in the next section, the binder also strongly affects the behavior of the carbon electrodes and this may be partly attributed to an impact on the surface chemistry, as will be discussed.

Figure 7 compares two FT–IR spectra obtained from KB–Teflon electrodes polarized in MF–LiAsF$_6$ solutions under argon and CO$_2$ atmospheres (Figs. 7(a) and 7(b), respectively). Spectrum 7(a) has both Li formate and Li alkoxy (probably LiOCH$_3$) peaks formed by MF reduction according to Scheme 1. Spectrum 7(b) also has strong Li$_2$CO$_3$ peaks in addition to the expected Li formate peaks. Hence, CO$_2$ dissolved in

SOLVENT REDUCTION

(PC) $\qquad$ $\xrightarrow{e^-}$ $\qquad$ PC Radical Anion

(structure: $CH_3-CH-CH_2$ carbonate $\xrightarrow{e^-}$ $CH_3-\dot{C}H-CH_2$ radical anion)

$$2\ PC^{\cdot -} \longrightarrow CH_3-CH(^-O_2CO)-CH_2(OCO_2^-) + CH_3-CH=CH_2\uparrow$$

$$\downarrow 2Li^+$$

(Li alkylcarbonate) $CH_3CH(OCO_2Li)\ CH_2(OCO_2Li)\downarrow$

SALT REDUCTION

$$LiClO_4 + Xe^- + 2\ X\ Li^+ \longrightarrow Li_2O\downarrow + LiClO_3\downarrow \text{ or } LiClO_2\downarrow$$

$$\text{or} \qquad \text{or}$$

$$LiClO_4\downarrow \qquad LiCl\downarrow$$

$$LiAsF_6 + 2e^- + 2Li^+ \longrightarrow 3LiF\downarrow + AsF_3$$

$$AsF_6 + 2e^- + 2XLi^+ \longrightarrow Li_xAsF_{3-x}\downarrow + XLiF\downarrow \qquad ?$$

CONTAMINATION REDUCTION

$$\tfrac{1}{2}O_2 + 2e^- + 2Li^+ \longrightarrow Li_2O\downarrow$$

$$H_2O + e^- + Li^+ \longrightarrow LiOH\downarrow + \tfrac{1}{2}H_2\uparrow$$

$$2CO_2 + 2e^- + 2Li^+ \longrightarrow Li_2CO_3 + CO$$

A SECONDARY REACTION

$$2ROCO_2Li + H_2O \longrightarrow 2ROH + CO_2 + Li_2CO_3\downarrow$$

Scheme 2. Basic surface chemistry of lithium and noble metal electrodes at low potentials in propylene carbonate (PC) solutions of lithium salts. (Proven by FT–IR, XPS and X-ray microanalysis [11–19].)

MF reacts on carbon similarly to its reaction on Li or noble metals at low potentials in the presence of Li salt to form Li_2CO_3. A proposed mechanism for this reaction has already been discussed [14] (a coproduct of the CO_2 reaction is probably CO gas).

Hence, the improvement in the degree and reversibility of Li ions intercalation of the various carbons in MF–Li salt solutions containing CO_2 (as reported in the previous section) is due to Li_2CO_3 formation which probably passivates the carbon more effectively and prevents side reactions of solution species which interfere with Li–C intercalation.

As proven by previous studies [11–17] and shown in Scheme 2, $LiClO_4$ is reduced on Li to LiCl and Li_2O while $LiAsF_6$ is reduced to LiF, and probably to AsF_3. Our previous studies also showed that both ClO_4^- and AsF_6^- are reduced on nonactive metals (in the presence of Li^+) at potentials between 1.5 to 1 V (Li/Li^+) [14].

In a parallel study [18] we found evidence that AsF_3 is reduced on Li to some insoluble Li_xAsF_y species which show the typical As–F stretching peak around 710 cm^{-1}. The presence of the same peak in the spectra of Figs. 6 and 7 seems to
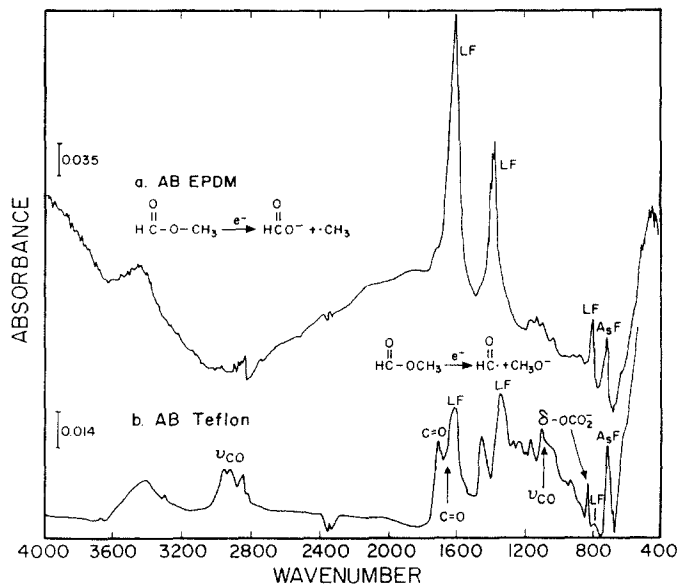
Fig. 6. Typical FT–IR spectra obtained *ex situ* from AB–EPDM (4%) and AB–Teflon (4%) after being polarized to 0.1 V in the MF–LiAsF$_6$ solutions. The electrodes were thoroughly washed (pure MF) and dried, then carbon particles were scraped from them and pelletized with KBr (transmittance mode). The proposed reaction schemes are also listed.

indicate that LiAsF$_6$ is reduced on carbon to form LiF and AsF$_3$ which is further reduced to insoluble Li arsenic fluoride species (see Scheme 2, [19]).

Ethers

Figure 8 shows a typical FT–IR spectrum obtained from graphite polarized in THF–1 M LiAsF$_6$ to low potentials (≈ 0.1 V versus Li/Li$^+$). As indicated, the spectrum has both alkoxy and As–F peaks. It was found that THF is reduced by Li to Li butoxide [15]. Hence, it seems that a similar THF reduction occurs on carbon. However, as shown in Fig. 3 (AB electrodes in galvanostatic charge/discharge cycling), the typical plateau in the first charge, which is attributed mostly to reduction of solution species, is obtained at potentials between 1 to 1.5 V. THF is reduced on nonactive metal at much lower potentials [15].

Since LiAsF$_6$ is reduced on noble metals (in the presence of Li$^+$) at potentials above 1 V (Li/Li$^+$) [11, 14, 15], it is very likely that an important part of the reduction processes indicated by the voltage plateaus in the first charging processes shown in Figs. 1, 2, 3, and 5 involves salt reduction (as indicated also by the strong As–F peak around 710 cm^{-1} in Fig. 8).

Alkyl carbonates

Figure 9 shows a typical FT–IR spectra, obtained from AB electrode cycled in PC–1 M LiAsF$_6$ solution, in the ATR mode. Spectrum 9(a) is related to the electrode before the electrochemical treatment. Spectrum 9(b) obtained from the electrode after being treated in solutions has all the typical PC peaks due to the residual solvent which is very difficult to remove due to its low volatility. However, the spectrum also has the typical carbonyl peak of ROCO$_2$Li species, which are the major PC reduction
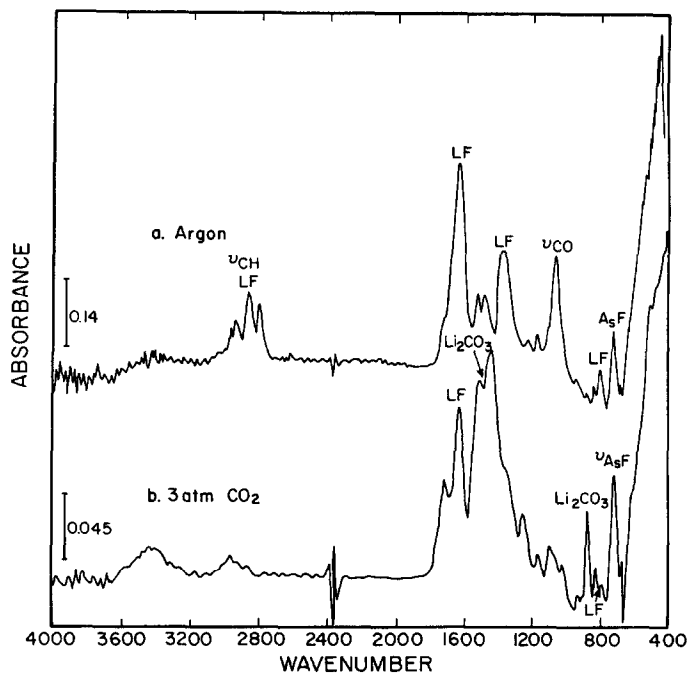
Fig. 7. Typical FT–IR spectra obtained *ex situ* from KB–Teflon (4%) electrodes polarized in MF–$LiAsF_6$ solutions to 0.1 V vs. Li/Li^+. Transmittance mode, carbon particles from the electrodes were pelletized with KBr (after being washed and dried); (a) the electrochemical treatment was under argon atmosphere, and (b) the electrochemical treatment was under CO_2 (3 atm).
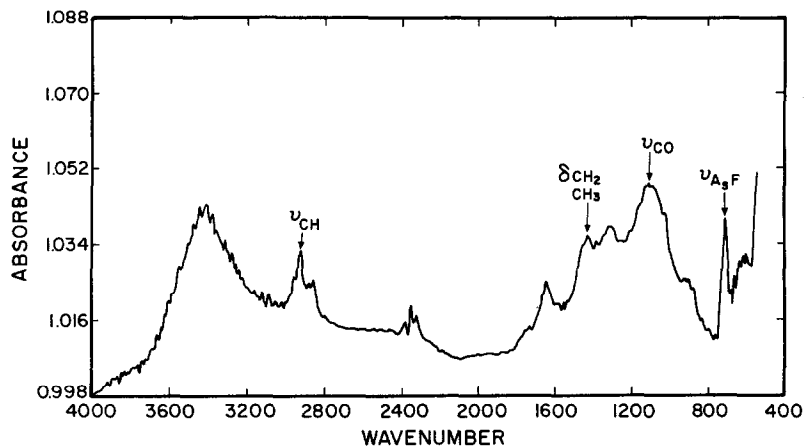

Fig. 8. A typical FT–IR spectrum obtained *ex situ* from a graphite–Teflon (4%) electrode polarized in THF–1 M $LiAsF_6$ solutions to 0.1 V. Transmittance mode, carbon particles pelletized with KBr.
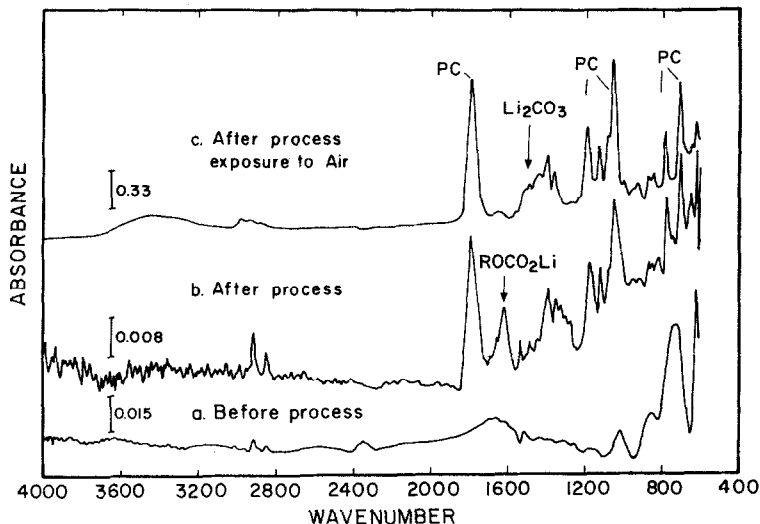
Fig. 9. Typical FT–IR spectra obtained from AB–EPDM (4%) electrodes cycled in PC–1 M LiAsF$_6$ solution (galvanostatic processes between 0.1 and 1.5 V vs. Li counter electrodes). After being washed and dried the electrode was measured using ATR mode, pressed to a ZnSe prism; (a) electrode before the process, (b) electrode after the electrochemical treatment, and (c) electrode was further exposed to humid air before the measurement.

products by Li, around 1640–1650 cm^{-1}. These species react readily with trace water to form Li$_2$CO$_3$, CO$_2$ and ROH [15].

Indeed, when the same electrode was exposed to humid air, followed by FT–IR measurement, spectrum 9(c) was obtained in which the ROCO$_2$Li peaks disappeared and a new Li$_2$CO$_3$ peak appears (around 1500–1400 cm^{-1}, as shown in Fig. 9). Hence, PC is reduced on carbon at low potentials (in the presence of Li salt) to ROCO$_2$Li species (similar to its reduction by Li). A proposed mechanism is suggested in Scheme 2 based on previous studies [12].

Figure 10 presents three FT–IR spectra obtained from graphite electrodes treated in THF, PC and THF–PC 1:1 solutions of 1 M LiAsF$_6$ (Figs. 10(a)–(c), respectively). The spectra of Fig. 10 were obtained using diffuse reflectance mode and the peak intensities are presented in Kubelka Munk units [20]. This mode of operation enables the direct measurement of reflectance of IR from the carbon particles, and therefore seems to be ideal for the study of surface species formed on carbon. Due to the spectral properties of the carbon particles, the spectra obtained using this mode are of poor resolution and the bands are broad. Nevertheless, the spectra obtained include significant information, and the masking effect of PC is much less of a problem than in the other modes (e.g., ATR, Fig. 9). Spectrum 10(a) related to THF has mostly alkoxide species around 1450–1350 cm^{-1} (δCH$_2$, CH$_3$), 1100–1000 cm^{-1} (νC$-$O), 800–750 cm^{-1} (νC$-$C) and 600–550 (νO$-$Li).

Spectrum 10(b) related to PC has the typical carbonyl peak of ROCO$_2$Li around 1650–1630 cm^{-1}. Spectrum 10(c) related to PC–THF mixture seem to be a superposition of spectra 10(b) and 10(a) and shows, therefore, that both THF and PC reduction contribute to the build-up of surface films on the carbon when treated in this solvent mixture.
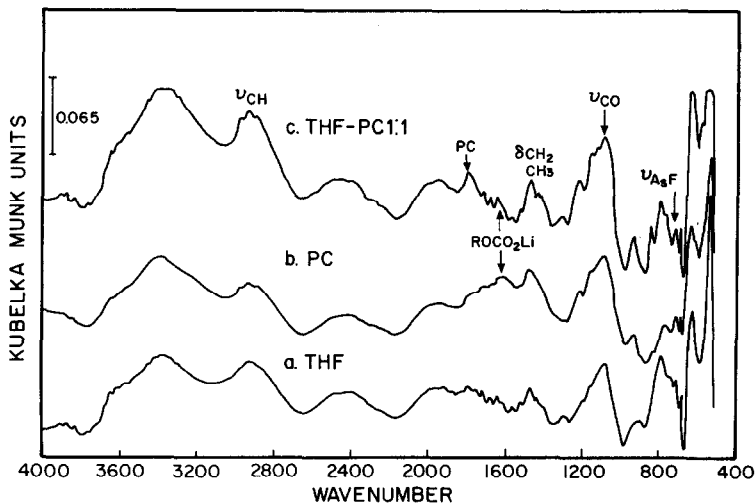
Fig. 10. Typical FT–IR spectra obtained *ex situ* from graphite–Teflon (4%) electrodes treated in various 1 M LiAsF$_6$ solutions. Carbon particles were scraped from the electrodes and measured using diffuse reflectance mode. The electrodes were cycled galvanostatically 10 times between 0.05 and 1.5 V vs. Li counter electrode; (a) THF, (b) PC, and (c) THF–PC 1:1.

These observations are in line with previous studies related to Li electrodes in solvent mixtures [21], and which prove that the surface films formed on Li in ether–alkyl carbonate mixtures are composed of reduction products of both solvents.

The effect of the binder

Figure 11 presents the voltage–time behavior of three graphite electrodes, with different binders. The three electrodes are cycled in MF–1 M LiAsF$_6$ solution under CO$_2$ atmosphere (6 atm), and they behave quite differently from each other. The highest degree of reversible intercalation is obtained when the binder is PVDF. Graphite–Teflon electrodes also behave reversibly. In contrast, the electrodes prepared with EPDM as a binder behave irreversibly and the charge involved in the first charge is smaller than what would be expected for Li–C intercalation and the solution side reactions occurring in this cathodic process. It seems that EPDM is not a suitable binder for intercalation electrodes, while Teflon and PVDF are adequate.

In other experiments, the influence of the amount of Teflon binder in the electrodes on their performance was explored. It was found that an optimum is obtained at 4–5 wt.% binder in the carbon and as the amount of the binder increases, the reversibility of the intercalation-deintercalation process decreases.

The influence of the binder on the electrode's behavior is explained as follows: Since the electrodes are composed of carbon particles bound by polymer particles, the solvent can creep around the carbon surface embedded in the binder and react at low potential (as was indeed proven in this work). These solvent reactions on the carbon surface precipitate films which are electrical insulators (as evidenced by the fact that they passivate the electrodes and the solution reduction only occurs in the first charging process). Therefore, these surface films may electrically disconnect carbon particles from the bulk in a similar way to which Li dendrites formed on Li metal during Li deposition are disconnected electrically from the anode in prolonged charge/discharge cycling [22].
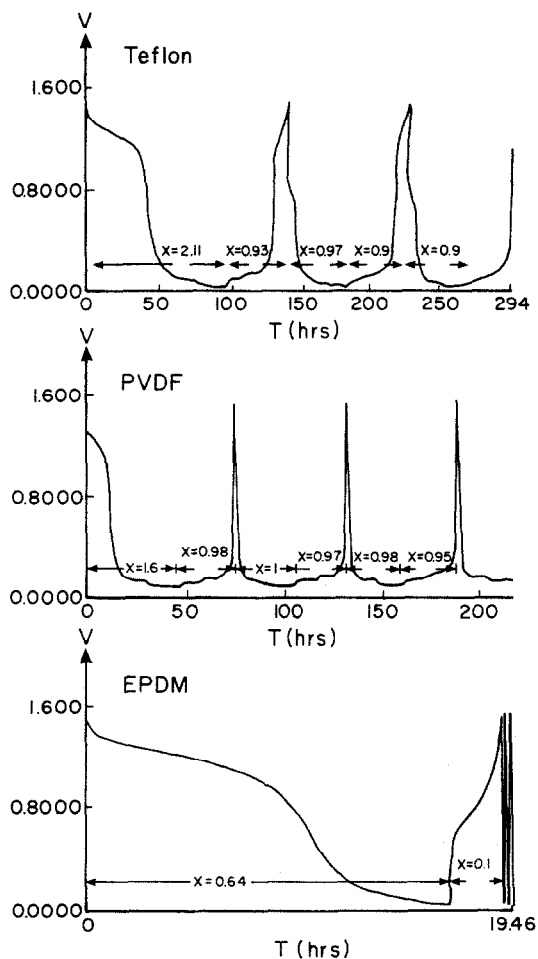
Fig. 11. The typical voltage–time behavior of graphite electrodes with three different binders (as indicated), cycled galvanostatically between two voltage limits (0.05 and 1.5 V vs. Li counter electrode) in MF–1 M LiAsF$_6$ solution under CO$_2$ pressure (6 atm). The charges involved are expressed in equivalents per 6 moles of carbon (x in Li$_x$C$_6$).

PVDF and Teflon have fluorinated carbons which react readily with Li to form LiF and lithiated carbon species. It is quite possible, therefore, that both polymers can be partly reduced at low potentials in the presence of Li cations on the carbon–polymer interface.

Such processes may stabilize the carbon particles in the matrix in which they are embedded and block the carbon–polymer interface and in this way prevent solvent reactions on the carbon surface, which, as discussed above, can disconnect carbon particles from the bulk.

Such a stabilization, occurring when fluorinated polymers are used as binders, may keep most of the carbon particles in electrical contact with the bulk and enables efficient electrochemical interaction of the carbon with the solution.

Conclusion

Lithium may intercalate reversibly with synthetic graphite at a stoichiometry close to LiC_6, in polar aprotic solvents containing Li salts. However, the degree of intercalation and its reversibility is strongly affected by the solvent system used. The best results were obtained in MF–$LiAsF_6$ or $LiClO_4$ solutions under CO_2 atmosphere (3–6 atm).

The presence of CO_2 is critical for obtaining reversible intercalation and a flat potential profile (Fig. 11). Some reversible Li intercalation is obtained with graphite also in ethers (e.g., THF, and 1,3-dioxolane), but its extent is far from the expected stoichiometry of LiC_6. When PC is present in solutions, either as a major or cosolvent, no Li intercalation could be obtained with the graphite type used.

Some degree of reversible intercalation (stoichiometry of $Li_{0.3-0.5}C_6$) is also obtained with AB and carbonized PAN. In MF/CO_2 solutions Li could intercalate with PAN reversibly to an extent close to optimal ($Li_{0.8-1}C_6$). In general, the behavior of these carbons is less sensitive to the electrolyte used as compared with graphite.

The first charging of carbon with Li is accompanied by irreversible solvent and salt reduction which covers the carbon surfaces with passivating films. These films are similar in their chemical structure to those formed on Li in the same solutions. Thus, PC is reduced on carbon to $ROCO_2Li$ species, ethers are reduced to alkoxides, MF is reduced to Li formate, $LiAsF_6$ and $LiClO_4$ are reduced to Li halides and CO_2 reacts to form Li_2CO_3 (and probably CO). Their precipitation blocks the surface and prevents further solution reaction. The amount of surface species formed depends on the type of carbon, the reactivity of the solution and the passivating properties of its reduction products, and is not correlated directly to the surface area of the carbon.

It is suggested that as the carbon is more graphitic in structure, the degree of intercalation may be closer to the ideal and its potential profile may be lower and flat (and, therefore, more attractive for use as an anode), but it is more sensitive to solution composition. This may be due to exfoliation of the graphite planes because of cointercalation of solvent molecules and their possible reduction within the carbon structure. As the carbon is less graphitic and more amorphous (e.g. AB, carbon fibers), its interaction with Li ions is less influenced by the solution components since its structure is more stable. However, the degree of intercalation is then lower and the potential profile is less attractive since intercalation starts at relatively high potentials (Figs. 1 and 2).

This work obviously shows that the performance of carbon materials as alternative anodes for rechargeable Li batteries may be optimized by a proper choice of electrolyte solutions. The most important aspect of this optimization is to modify the surface chemistry of carbon in solutions by the use of proper additives which react on the surface to form better passivating species, (e.g., CO_2 which forms Li_2CO_3) and/or prevents solvent cointercalation (e.g., crown ethers).

This work seems to show that the carbon to choose for anode materials should have some intermediate structure between the highly-ordered graphite and the less ordered carbon blacks' structure. Such carbon may intercalate Li reversibly close to the optimal degree (LiC_6) and yet be stable in solutions and not as strongly affected by solution species as graphite.

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