Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of Power Sources 119–121 (2003) 504–510

JOURNAL OF POWER SOURCES

www.elsevier.com/locate/jpowsour

The study of capacity fading processes of Li-ion batteries: major factors that play a role

B. Markovsky[a], A. Rodkin[a], Y.S. Cohen[a], O. Palchik[a], E. Levi[a],
D. Aurbach[a,*], H.-J. Kim[b], M. Schmidt[c]

[a]*Department of Chemistry, Bar-Ilan University, 52900 Ramat-Gan, Israel*
[b]*Battery Research Institute, LG Chem. Research Park, 305-388 Tajeon, South Korea*
[c]*Merck KGaA, D-64293 Darmstadt, Germany*

Abstract

In this work, we studied the impact of some factors on the behavior of practical electrodes of Li-ion batteries. These included elevated temperatures (45–80 °C), prolonged storage of Li-ion cells, and additives in the electrolyte solution. The Li-ion battery systems studied included negative electrodes (anodes) comprising of mesocarbon microbeads (MCMB) and mesocarbon fibers (MCF), and Li_xCoO_2 positive electrodes (cathodes) in an ethylene carbonate (EC)/ethyl-methyl carbonate (EMC) (1:2)/$LiPF_6$ 1 M solution. Vinylene carbonate (VC) and a Li-organo-borate complex (Li-OBC) were tested as additives. It is shown that the electrochemical response of Li–C negative electrodes depends on the structure of the surface films controlling their behavior, which change upon storage, temperature, and cycling. We established that impedance of these electrodes increased with storage time due to the enrichment of the surface films by LiF and other fluorine-containing species. The capacity fading of the Li_xCoO_2 electrodes in cycling/storage processes at elevated temperatures relates mostly to surface phenomena, whereas the bulk structural characteristics of the electrodes do not change.

Keywords: Li-ion cells; Elevated temperatures; Storage; Capacity fading; Additives in solution

1. Introduction

There is no doubt that improving the performance of Li-ion batteries at elevated temperatures and understanding the mechanisms of their capacity fading are complicated and important problems of the field. Among the factors that influence the capacity of Li-ion batteries we can mention cycling rates, temperature, aging of the electrodes, prolonged storage (self-discharge), etc.

In recent years, we see in the literature more and more comprehensive reports on the study of aging of Li-ion batteries and their possible failure mechanisms [1,2]. For instance, we can mention a recent study of the failure of graphite electrodes at 80 °C, which involves a very high irreversible capacity [3]. Several research groups studied basic mechanisms of aging of rechargeable lithium batteries at elevated temperatures and the relative role of the negative and the positive electrodes in the overall capacity fading measured [4–6]. We can mention also reports on developments of protective treatments that improve the performance of cathodes (e.g. $LiMn_2O_4$) at elevated temperatures (>60 °C) [7].

In the present work, we studied the impact of some of the above-mentioned factors, such as temperature, storage conditions and additives in solutions, on the electrochemical performance and the surface reactions of graphite anodes and Li_xCoO_2 cathodes in Li-ion cells.

2. Experimental

Composite graphite and lithiated cobalt oxide Li_xCoO_2 electrodes (100–150 μm thick) used for this study were prepared at LG Chem Inc. The active mass of the anode was a mixture of mesocarbon microbeads (MCMB, 38%) and mesocarbon fibers (MCF, 56%). The load of the positive and the negative electrodes was around 23 and 10.5 mg/cm^2, respectively. We used electrolyte solutions comprising 1 M $LiPF_6$, ethylene carbonate (EC) and ethyl-methyl carbonate (EMC), 1:2 volume ratio with and without additives, prepared by Merck KGaA. As additives to the electrolyte solution, vinylene carbonate (VC) and a Li-organo-borate complex (Li-OBC)—denoted as Merck's

---

[*] Corresponding author. Tel.: +972-3-531-83-17;
fax: +972-3-535-12-50.
E-mail address: aurbach@mail.biu.ac.il (D. Aurbach).

0378-7753/03/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0378-7753(03)00274-X

additive AD25—were used. The electrochemical experiments were performed in specially designed three-electrode cells (Li metal counter and reference electrodes) of a parallel plate configuration made from polyethylene. All the potentials are given versus Li/Li$^+$. The equipment used for voltammetric and electrochemical impedance studies was a battery test unit model BTU-1470 from Solartron Inc. The instrumentation for the study of the electrodes' surface chemistry by XPS, FTIR and EDAX, their structural and morphological changes by XRD and SEM were described elsewhere [8,9].

3. Results and discussion

First, we did not find a pronounced temperature effect on the electrochemical behavior of the Li–graphite electrodes up to 45 °C. Surface films comprising mainly Li-alkyl carbonates, Li_2CO_3, LiF, Li_2O, LiOH, Li_xPF_y, and polymeric species are formed on the carbon anodes during a first cathodic polarization. The electrodes reach full passivation when polarized at rates $<C/5$ from OCV (around 3 V) to 0 V versus Li/Li$^+$ at temperatures below 45 °C. In contrast, at elevated temperatures (60–80 °C), it is much more difficult to stabilize and passivate carbon electrodes. For instance, upon voltammetric studies of carbon electrodes at temperatures below 45 °C, stabilization is reached within two CV cycles (e.g. in the potential range of 3–0 V and at scan rate of 2 mV/s). When the temperatures are too high (>60 °C), stabilization of graphite electrodes in CV cycling (same potential range and scanning rate) is reached only after a number of repeated CV cycles. Fig. 1 shows first voltammetric responses of composite (MCMB + MCF) electrodes in a solution of EC/EMC (1:2)/$LiPF_6$ at various temperatures. The main impact of high temperatures (>25 °C) on the electrochemical behavior of the negative electrodes is an increase in the charge involved in the irreversible reactions (peaks I and II), and a shift of the relevant peaks to more positive potentials with an increase of the temperature (Fig. 1). The irreversible reactions of solution species on the graphite electrode's surface are enhanced at elevated temperatures and lead to a poor surface passivation and a fast electrode's capacity fading.

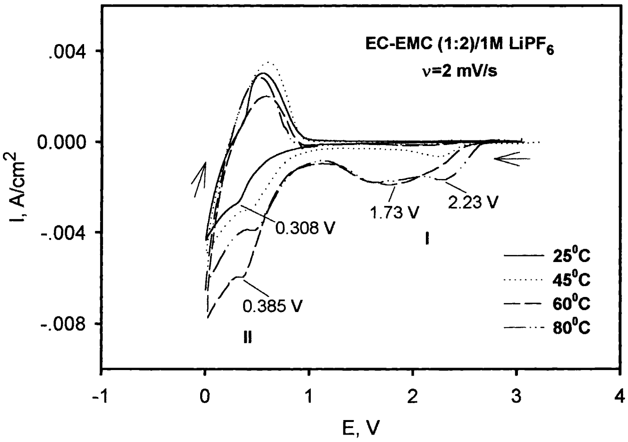

Fig. 1. First cyclic voltammograms (2 mV/s) measured with MCMB + MCF negative electrodes in an EC/EMC (1:2)/$LiPF_6$ solution at various temperatures, as indicated.

We conducted voltammetric studies of Li–carbon electrodes at 60 °C in additive-free solutions and in solutions containing VC- or Li-organo-borate complex (AD25), and found that the presence of the latter additive reduces substantially the irreversible capacity of these electrodes. It was clearly demonstrated that the presence of AD25 stabilizes graphite electrodes at elevated temperatures and improves their passivation [10]. Due to the limited volume allowed for this paper, it was impossible to present all the experimental data. However, our studies of the carbon electrodes at elevated temperatures can be summarized as follows.

1. The higher the temperature, the worse the electrode's passivation by surface films. This is reflected by the higher irreversible capacity measured as the temperature is higher, and the number of cycles required to stabilize the graphite electrodes (i.e. reaching cycling efficiency close to 100%).
2. When the electrodes are passivated at low temperatures, they are not necessarily stable at higher temperatures because the structure of the surface films, which passivate the carbon electrodes, strongly depends on the temperature. Surface films formed at low temperatures may allow electron transport through them at elevated temperatures and hence, further irreversible surface reactions. It was shown that the reversibility of graphite electrodes is worse when they are stabilized and cycled at 25 °C and the temperature is further raised to 60 °C.
3. Contaminants, such as HF, play a detrimental role in the electrodes' stabilization by surface films. Thereby, the higher the ratio between the electrodes' active mass and the solution volume, the better the stabilization of the carbon electrodes at elevated temperature. For instance, highly stable behavior of graphite electrodes could be obtained at 80 °C in coin-type cells testing, where the amount of solution is very small and hence the influence of contaminants, such as HF, is very low.
4. The additives used in this study, VC or AD25 have a positive impact on the Li-graphite electrodes' behavior, especially at elevated temperatures. They influence their surface chemistry and enhance the formation of passivating surface films [8,10].

When graphite electrodes are stored at constant potential (around 3 V) at any temperature, surface film *reformation* takes place. Surface films formed at low potentials dissolve when the electrodes are held at higher potentials (2–3 V). Also, secondary reactions between surface films and solution species take place, which change the structure of the surface films initially formed.

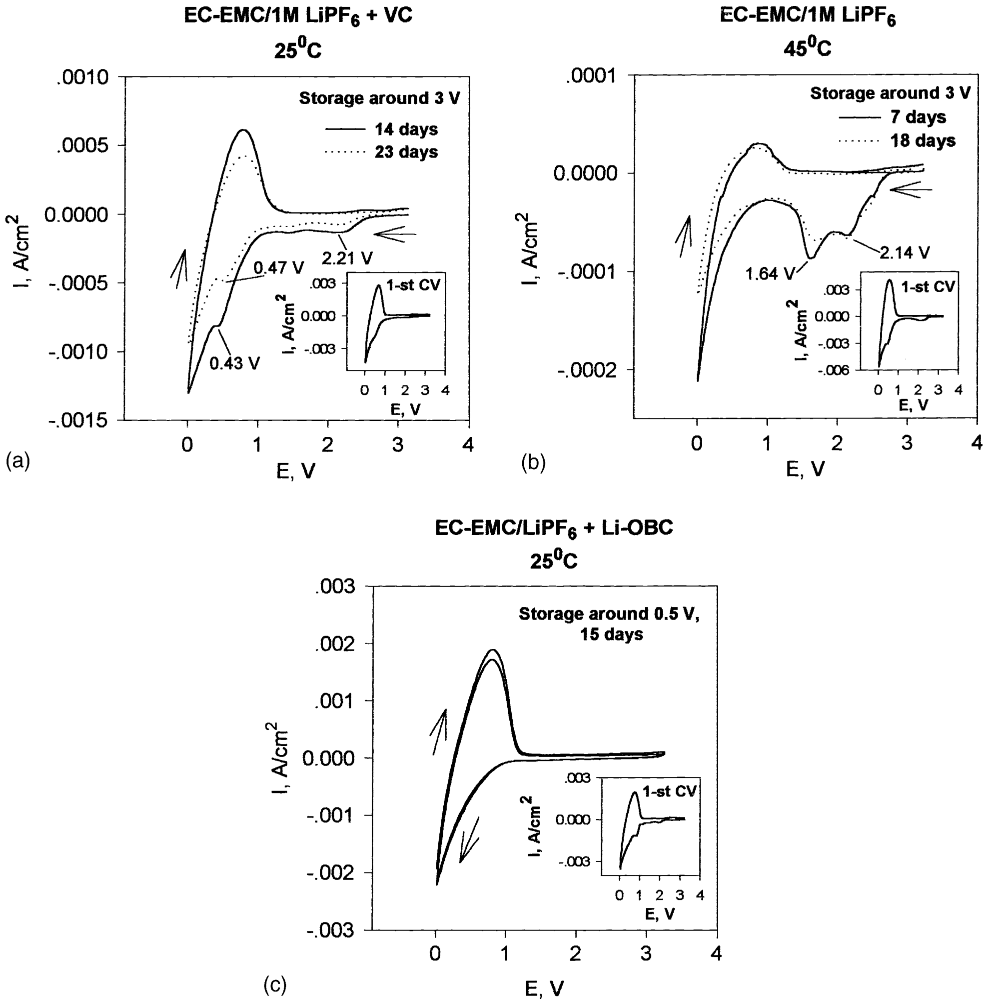

Fig. 2. First CVs (2 mV/s) measured with MCMB + MCF electrodes after storage in solutions, as indicated. The electrodes were initially cycled and hence their passivation was fully developed before storage at OCV. Insets: the 0-day data represented as first CVs recorded at 2 mV/s from the pristine MCMB + MCF electrodes.

For instance, polarization after storage of electrodes whose passivation was fully developed, leads to a *reformation* of surface films, as seen in the voltammetric response of graphite electrodes presented in Fig. 2a and b. It is clearly seen from the CVs recorded after storage of Li–graphite cells during 1–3 weeks that reduction of solution species takes place (at potentials <1 V) in the first cathodic sweep and new surface films are formed. The state-of-charge of the electrodes is a major factor that determines the stability of the surface films during storage, not less important than the solution composition or the temperature. For instance, voltammetric studies of electrodes stored at 0.5 V do not show cathodic currents related to reduction of solution species (Fig. 2c). At the same time, *reformation* of the surface films is clearly seen in voltammetric studies of electrodes stored for several days around 3 V after their passivation was fully developed (by polarization to 0 V) before storage. This means that upon storage at OCV the passivation is broken down. We attribute this to partial dissolution and rearrangement of the surface films during prolonged storage.

It is well known that polarization of graphite electrodes in alkyl carbonate solutions leads to solvent reduction, which forms $ROCO_2Li$ surface species. However, the carbonates thus formed are not stable in the $LiPF_6$ solutions due to their reactions with HF. Reduction products of $LiPF_6$ become the dominant species on the electrodes surfaces during prolonged storage in $LiPF_6$ solutions. Below we list some possible surface reactions of the carbon electrodes, which lead to the formation of LiF and other fluorine-containing species [11]:

$$LiPF_6 \rightarrow LiF + PF_5$$

$$PF_5 + H_2O \rightarrow HF + PF_3O$$

$$PF_5 + ne^- + nLi^+ \rightarrow LiF + Li_xPF_y$$

$$PF_3O + ne^- + nLi^+ \rightarrow LiF + Li_xPF_yO$$

During prolonged storage, LiF replaces the surface carbonates initially formed. Hence, the surface film on the anode becomes rich in LiF species, which are known to be

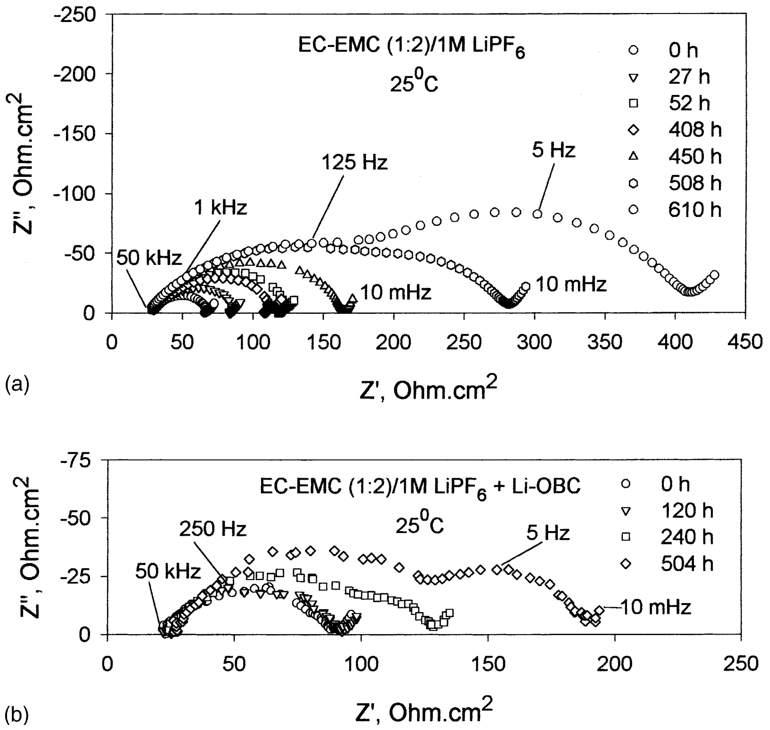

Fig. 3. Electrochemical impedance data presented as Nyquist plots obtained from MCMB + MCF electrodes at $E = 170$ mV vs. Li/Li$^+$ in an additive-free solution and in a solution containing Li-organo-borate complex after prolonged storage, as indicated.

very resistant to Li-ion migration through them [12]. Thereby, the above processes lead to a considerable increase of the impedance of the graphite anodes during prolonged storage as demonstrated in Fig. 3. It was also found that prolonged storage of the lithiated graphite electrodes both in the additive-free and additive-containing solutions resulted in much more sluggish electrode kinetics compared to the pristine electrodes. This is due to a drastic increase of the charge-transfer resistance expressed as a semicircle in the medium-to-low frequency domain of the impedance spectra presented as Nyquist plots.

LiF formation on the graphite electrode surfaces during prolonged storage was unequivocally demonstrated by X-ray diffraction (XRD) studies. XRD patterns measured from stored graphite electrode (Fig. 4) clearly show the appearance of a new peak of lithium fluoride (griceite) around $2\theta = 38.6^{\circ}$. We could carry out semi-quantitative analysis of graphite electrodes from their XRD patterns. For instance, graphite electrode cycled 20 times in EC/EMC/LiPF$_6$ solution can accumulate 4 wt.% surface LiF. Storage of the cycled electrodes during several weeks increases the LiF content by a factor of 3, due to the above-mentioned reactions. From the half-width of the LiF peaks, we could estimate the average size of the lithium fluoride grains, which belong to the surface films. It is usually around 10–20 nm initially, and increases to 100 nm upon prolonged storage. According to an elemental surface analysis (EDAX), the fluorine/carbon ratio on the surface of cycled and stored electrodes may be as high as 5. It should be noted that, in general, the presence of either VC or AD25 in solutions suppresses formation of surface LiF on graphite electrodes. This was confirmed in the present work by analyzing cycled electrodes using XPS. The fluorine spectra of electrodes cycled in VC- or AD25-containing solutions demonstrated much smaller (by factors of 2–5) LiF peaks (binding energy about 685 eV) compared to the spectra measured for electrodes cycled in additives-free solutions.

A similar trend of increasing electrode impedance during prolonged storage at elevated temperatures (as was found with Li–graphite electrodes) was also found with Li$_x$CoO$_2$

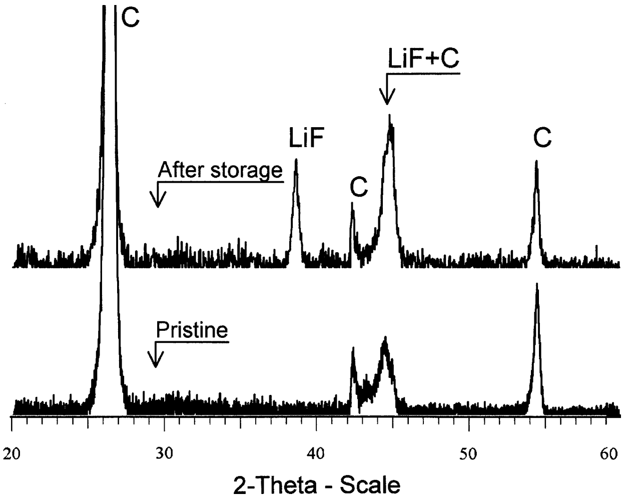

Fig. 4. XRD patterns of powders scraped from a pristine MCMB + MCF electrode and an electrode after cycling and storage (35 days at OCV, $E = 170$ mV) in EC/EMC (1:2)/1 M LiPF$_6$ solution.

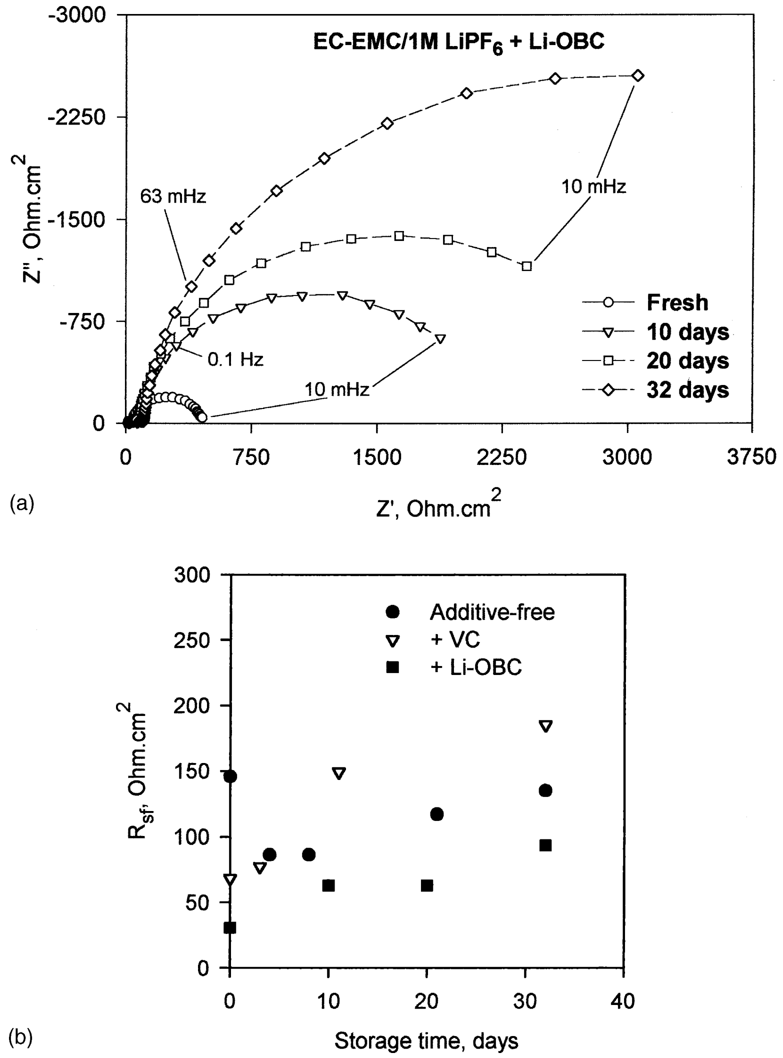

Fig. 5. Typical impedance spectra presented as Nyquist plots: (a) obtained with Li_xCoO_2 electrodes at $E = 3.87$ V vs. Li/Li^+ in an additive-containing solution after prolonged storage, as indicated; (b) dependence of the surface film resistance R_{sf} of Li_xCoO_2 electrodes on the storage time.

electrodes. Fig. 5a presents impedance spectra measured from Li_xCoO_2 electrodes in additive-containing solution. From our studies it is clear that Li_xCoO_2 electrodes also develop surface films and their impedance increases during prolonged storage. The presence of VC or AD25 in solutions decreases the surface film resistance of pristine electrodes (especially significant when the solutions contain AD25).

In Fig. 5b, we show the resistance of the surface films (R_{sf}) formed on Li_xCoO_2 electrodes, as a function of storage time (the values of R_{sf} are calculated from the diameter of the high-frequency semicircle in the impedance spectra presented as Nyquist plots). As seen, the surface films resistance of pristine electrodes is the largest in the additive-free solution, whereas R_{sf} of the Li_xCoO_2 electrodes is the smallest in the solution containing the Li-organo-borate additive for both fresh electrodes and electrodes after prolonged storage.

It was generally found that the surface films on Li_xMO_y electrodes (M: Mn, Ni, Co, V) may comprise species such as $ROCO_2Li$ (which are the products of possible nucleophilic reactions between the lithiated metal oxide and alkyl carbonate molecules), LiF (a product of the acid–base reaction between Li_xMO_y and trace HF) and polycarbonates (formed by polymerization of solution species induced by acidic species or the positively charged cathodes) [13]. We assume that the presence of the Li-organo-borate complex (AD25) in solutions results in the formation of stable and steady surface film on the Li_xCoO_2 electrodes, which is less resistive to Li-ion migration through it, in comparison with surface films formed in the additive-free or VC-containing solutions. It was demonstrated also that in the AD25-containing solution, the Li_xCoO_2 electrodes' kinetics is faster, and the capacity loss upon cycling after prolonged storage at 60 °C is the smallest, 3% compared to 14–15% in additive-free solutions or solutions containing VC. It should be noted that cycling and prolonged storage of the Li_xCoO_2 electrodes at elevated temperatures (e.g. 60 °C) do not influence their basic 3D structure, as it is clearly evidenced from XRD studies

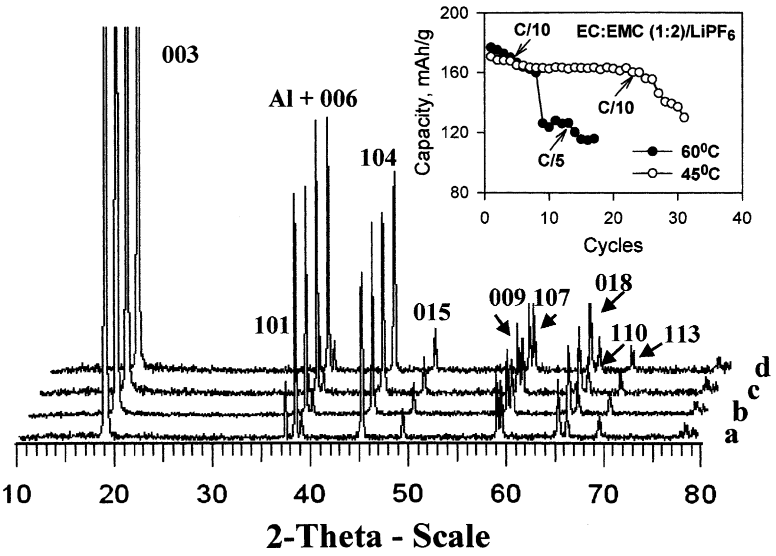

Fig. 6. XRD patterns of Li_xCoO_2 electrodes: (a) pristine electrode (as-received from LG Chem.); (b) cycled in EC/EMC (1:2)/1 M $LiPF_6$ solution at 60 °C and stored for 7 days around 4.0–4.1 V; (c) cycled in EC/EMC (1:2)/1 M $LiPF_6$ solution at 60 °C and stored for 32 days around 4.0–4.1 V; (d) cycled in EC/EMC (1:2)/1 M $LiPF_6$ solution containing AD25 at 60 °C and stored for 32 days around 4.0–4.1 V. Inset: results of galvanostatic cycling (*C*/5 and *C*/10 rates) of Li_xCoO_2 electrodes in coin-type cells with Li counter electrode at 45 and 60 °C, EC/EMC (1:2)/1 M $LiPF_6$ solution.

(Fig. 6). The comparison of XRD patterns of cycled Li_xCoO_2 electrodes presented in Fig. 6 demonstrates that both the intensity of the diffraction peaks and their positions do not change with storage and cycling of the electrodes. Hence, we can conclude that the increase in the positive electrodes' impedance during cycling and storage is caused mainly due to surface reactions and not due to changes in the electrodes bulk structure.

We found that cobalt ions dissolve from Li_xCoO_2 cathodes into the electrolyte solutions during cycling and prolonged storage. However, this Co ion dissolution does not influence at all the bulk structural characteristics of the electrodes. It was demonstrated that cobalt is deposited on the lithium anodes in Li/Li_xCoO_2 cells as detected by EQCM and XPS studies [14].

The presence of the Li-organo-borate complex in solutions *prevents* deposition of cobalt on the anodes in Li/Li_xCoO_2 cells. This finding is another interesting evidence to the pronounced influence of the presence of this additive in solutions on the surface chemistry of Li or Li–graphite electrodes [14].

4. Conclusions

i. We found that during storage of graphite electrodes at constant potentials (around 3 V), surface films rearrangements and *reformation* take place. This can be related to partial dissolution and secondary reactions of the initially formed surface films. The state-of-charge/discharge of the lithiated graphite electrodes is a major factor determining the stability of the surface films during prolonged storage.

ii. A continuous increase in the impedance of Li–graphite electrodes in EC/EMC/$LiPF_6$ solutions during prolonged storage is attributed to the enrichment of the surface films by LiF and other fluorine-containing species due to secondary reactions, as proved by X-ray diffraction and EDAX studies.

iii. Upon cycling/storage of Li_xCoO_2 electrodes at elevated temperatures, their bulk structural properties do not change. However, surface reactions of Li_xCoO_2 with solution species form surface films, which increase the electrode impedance. It appears that the capacity fading of Li_xCoO_2 electrodes during prolonged cycling, especially at elevated temperatures, relates mostly to surface phenomena such as the formation of surface films that cover the Li_xCoO_2 particles and may electrically isolate them from each other and from the current collector.

iv. Cobalt ions dissolve from the Li_xCoO_2 electrodes during their repeated cycling and storage in EC/EMC/$LiPF_6$ solutions and react at the negative electrode surface (cobalt deposition on the Li electrode was detected). The presence of the Li-organo-borate complex in solutions prevents cobalt deposition on the negative electrodes in Li/Li_xCoO_2 cells.

References

[1] C. Jehoulet, P. Biensan, J.M. Bodet, M. Broussely, C. Moteau, C. Tessier-Lescourret, in: Proceedings of the 192nd ECS Meeting, vol. 97, No. 2, Paris, 1997, p.153.

[2] S. Herreyre, O. Huchet, S. Bausseau, F. Perton, J.M. Bodet, Ph. Biensan, J. Power Sources 97–98 (2001) 576.

[3] A. Anderson, K. Edstrom, J. Thomas, J. Power Sources 81–82 (1999) 8.

[4] E. Wang, D. Ofer, W. Bowden, N. Iltchev, R. Moses, K. Brandt, J. Electrochem. Soc. 147 (2000) 4023.
[5] I. Bloom, B.W. Cole, J.J. Sohn, S.A. Jones, E.G. Polzin, V.S. Battaglia, G.L. Henriksen, C. Moltoch, R. Richardson, T. Unkelhaeuser, D. Ingersoll, H.L. Case, J. Power Sources 101 (2001) 238.
[6] F. Joho, B. Rykart, A. Blome, P. Novak, H. Wilhelm, M.E. Spahr, J. Power Source*s* 97–98 (2001) 78.
[7] S.-C. Park, Y.-M. Kim, S.-C. Han, S. Ahn, C.-H. Ku, J.-Y. Lee, J. Power Sources 107 (2002) 42.
[8] D. Aurbach, K. Gamolsky, B. Markovsky, Y. Gofer, M. Schmidt, U. Heider, Electrochim. Acta 47 (2002) 1423.
[9] D. Aurbach, B. Markovsky, A. Rodkin, M. Cojocaru, E. Levi, H.-J. Kim, Electrochim. Acta 47 (2002) 1899.
[10] D. Aurbach, K. Gamolsky, M. Koltypin, B. Markovsky, M. Schmidt, U. Heider, ITE Battery Lett. 2 (2001) 363.
[11] D. Aurbach, J. Power Sources 89 (2000) 206.
[12] D. Aurbach, B. Markovsky, A. Schechter, Y. Ein-Eli, H. Cohen, J. Electrochem. Soc. 143 (1996) 3809.
[13] D. Aurbach, K. Gamolsky, B. Markovsky, G. Salitra, Y. Gofer, J. Electrochem. Soc. 147 (2000) 1322.
[14] D. Aurbach, B. Markovsky, A. Rodkin, E. Levi, Y.S. Cohen, H.-J. Kim, M. Schmidt, Electrochim. Acta 47 (2002) 4291.