



On the capacity fading of LiCoO_2 intercalation electrodes: the effect of cycling, storage, temperature, and surface film forming additives

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Abstract

The electrochemical behavior and surface chemistry of LiCoO_2 intercalation cathodes as a function of cycling and storage at 25, 45, and 60 °C was studied. The standard solutions for this work comprised ethylene carbonate (EC), ethyl-methyl carbonate (EMC), (1:2) and 1 M LiPF_6 . The effect of two surface film-forming additives, vinylene carbonate (VC) and an organo-borate complex (denoted as Merck's AD25) in solutions was also explored. We analyzed temperature-dependent processes of surface film formation on the cathodes, which increase their impedance upon cycling and storage, thus making their electrochemical kinetics sluggish. We also analyzed cobalt dissolution from the cathodes at 25, 45 and 60 °C. The apparent capacity fading of the LiCoO_2 electrodes is attributed mostly to changes on their surface, rather than to bulk degradation. There are signs that the presence of HF in solutions may play a major negative role. Hence, as the electrode's surface/solution volume ratio is higher, the capacity fading of the LiCoO_2 electrodes should be lower. The main tools for this study were cyclic voltammetry, chronopotentiometry, impedance spectroscopy, electrochemical quartz crystal microbalance (EQCM), IR-spectroscopy, XRD, XPS, and SEM. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

One of the greatest successes of modern electrochemistry is the development and commercialization of Li-ion batteries. These batteries are rechargeable and possess the highest energy density available today for secondary battery systems ($> 150 \text{ W h/Kg}$) [1]. The anodes in these batteries are carbonaceous materials that can reversibly and electrochemically insert lithium. The most commonly used anodes are graphitic carbons with a capacity approaching a theoretical value of 372 mA h/g (LiC_6) [2]. The electrolyte solutions usually comprise mixtures of ethylene carbonate (EC) with dimethyl carbonate

(DMC), diethyl carbonate (DEC), or ethyl-methyl carbonate (EMC), and LiPF_6 as the salt [3]. These components of the electrolyte solutions for Li-ion batteries were selected after 30 years of R&D related to secondary Li battery systems. The alkyl-carbonates have a wide electrochemical window ($> 4.5 \text{ V}$) [4], and are apparently stable with lithium, lithiated carbons, and all relevant cathode materials (in the potential range of 2.0–4.5 V vs. Li/Li^+). It should be noted that on a thermodynamic basis, all the alkyl carbonate solvents should be reduced by lithium or lithiated carbons to form organic and inorganic carbonates (ROCO_2Li , Li_2CO_3). Lithium or lithiated carbons are apparently stable in these solvents only due to passivation phenomena [5]. The reduction products of these solvents precipitate as surface films that cover the electrodes and block a further electron transfer from Li or Li-C to

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solution species. Fortunately, due to the intrinsic properties of Li salts when precipitated as thin surface films, Li-ion transport is possible through these passivating surface layers when an electric field is applied [6]. LiPF_6 was selected as the preferred salt for Li-ion batteries because its solutions are highly conductive, its thermal stability seems to be better than other relevant Li salts such as LiClO_4 . Moreover, LiPF_6 is much more environmentally friendly than Li salts such as LiAsF_6 , and it can be distributed at a reasonable price. However, this salt is also reactive with lithium and lithiated carbon, and can be reduced to LiF and Li_xPF_y species [7]. It also decomposes to LiF and PF_5 [8]. The latter species react readily with protic species or groups to form HF , and hence, a LiPF_6 solution always contains HF contamination. However, in spite of these problems, LiPF_6 still rivals other relevant salts as the most commonly used electrolyte for Li-ion batteries.

The cathode materials for Li-ion batteries are usually lithiated transition metal oxides, which undergo reversible electrochemical Li intercalation–deintercalation processes in polar aprotic Li salt solutions. The most commonly used cathode material for commercial Li-ion batteries is LiCoO_2 . Completed delithiation–lithiation processes of this compound involve 270 mA h/g [9].

The major practical process occurs at 4 V and involves the exchange of $\frac{1}{2}$ Li per CoO_2 unit via a first order phase transition [10]. Another exchange of $\frac{1}{2}\text{Li}$ per CoO_2 unit ($\text{Li}_{0.5}\text{CoO}_2 \rightleftharpoons \text{CoO}_2 + \frac{1}{2}\text{e}^- + \frac{1}{2}\text{Li}^+$) occurs at potentials between 4.0 and 4.2 V (Li/Li^+) via the formation of a solid solution [11]. Although there are reports in the literature on Li-ion batteries that deliver many hundreds of full depth of discharge (DOD) charge–discharge cycles, many studies of practical Li-ion batteries comprising LiCoO_2 cathodes show that these batteries suffer from capacity fading upon cycling, especially at elevated temperatures.

The present work involves a study of the electrochemical behavior of LiCoO_2 electrodes at different temperatures and storage conditions in a selected standard solution of practical importance, namely, EC–EMC/ LiPF_6 . The goal of this study was to better understand possible capacity fading mechanisms of the LiCoO_2 electrodes upon cycling and during storage. We explored the effect of two film-forming additives in solutions, namely, vinylene carbonate (VC) and an organo-borate complex (denoted as Merck's AD25). The tools for this study included XRD and SEM for structural and morphological analysis, XPS and FTIR for surface analysis, and electrochemical techniques, such as cyclic voltammetry, chronopotentiometry, impedance spectroscopy, and electrochemical quartz crystal microbalance (EQCM).

2. Experimental

LiCoO_2 electrodes comprising active mass (95%), a PVdF binder (2.5%) and carbon black Super P (a conductive additive, 2.5%), on both sides of an aluminum foil (0.03 mm) current collector were obtained from LG Chem. The thickness of the electrodes was around 120–150 μm , their mass and geometric surface area exposed to the electrolyte solution were 41–42 mg and 1.80 cm^2 , respectively. LiCoO_2 electrodes were also prepared from Merck's (KGaA) LiCoO_2 , PVdF, synthetic graphite particles and aluminum foil, as already described [12]. The concentrations of additives, vinylene carbonate and Merck's AD25 organo-borate complex in the EC–EMC (1:2)/ LiPF_6 solutions were 5 and 1% by weight, respectively. For electrochemical measurements, we used polypropylene cells, including LiCoO_2 cathodes and lithium foil counter electrodes in parallel plate configuration, and Li wire reference electrodes [13]. All the potentials are given versus Li/Li^+ . XRD was measured ex-situ using an Advance-8 system model from Bruker, Inc. XPS data were obtained with an HX Axis system from Kratos, Inc. SEM measurements were carried out using a JEOL model JSM-840 scanning electron microscope, and FTIR measurements of the LiCoO_2 electrodes were performed ex-situ in diffuse reflectance mode (DRIFT) using a Nicolet, Inc. Magna model 860, FTIR spectrometer, placed in a home made glove box which provides an H_2O and CO_2 -free atmosphere, as already reported [14,15]. The electrochemical measurements included cyclic voltammetry and impedance spectroscopy (battery test unit model 1470 coupled with a FRA model 1255, the Cell Test software from Solartron, Inc.), and galvanostatic cycling (Maccor, Inc. model 2000, multichannel battery tester) [16]. The impedance of LiCoO_2 cathodes was measured in the 50 kHz–10 mHz frequency range at OCV conditions after prolonged polarization to predetermined potentials. The alternating voltage amplitude was 3 mV. EQCM measurements were performed using equipment from Elchema, Inc. (quartz crystals, 10 microns thick, AT cut, on which nickel was deposited) and specially designed cells, as already described [17]. All the measurements were carried out in home made thermostats at 25, 45, and 60 ± 0.5 °C. Electrolyte solutions, after cycling and storage experiments, were analyzed for cobalt content by the inductive coupled plasma (ICP) technique (ICP-AES, model 'Spectroflame Modula E' from Spectro, Kleve, Germany).

3. Results and discussion

Figs. 1 and 2 show cyclic voltammograms of lithiated cobalt-oxide electrodes measured in standard solutions and solutions containing VC or AD25 (indicated) at 25

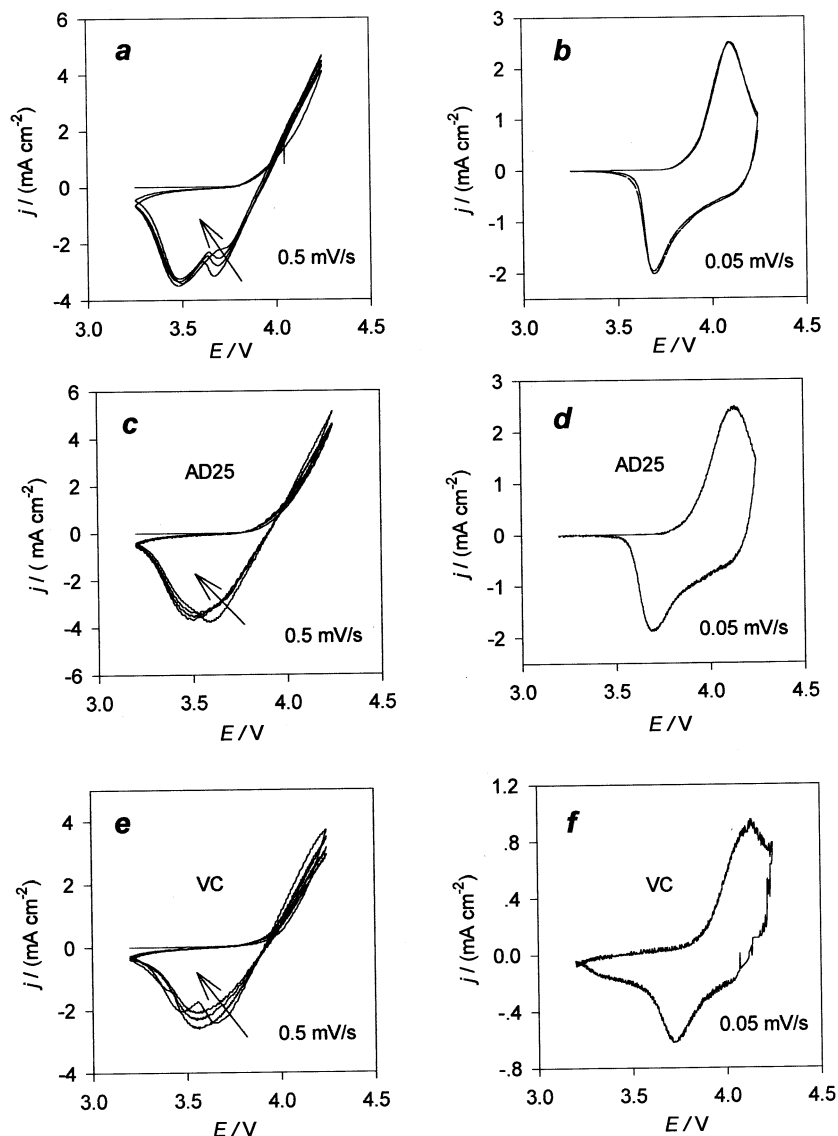


Fig. 1. Cyclic voltammograms measured at 25 °C with LiCoO₂ electrodes in EC–EMC (1:2)/LiPF₆ mother solutions (a, b), and in solutions containing AD25 (c, d) and VC (e, f). Potential scan rates are indicated.

and 60 °C, respectively (potential range of 3.25–4.25 V vs. Li/Li⁺). These figures present voltammograms measured at $\nu = 0.5$ and 0.05 mV/s, as indicated. The voltammograms measured at 0.05 mV/s at 25 °C (Fig. 1) are characterized by two corresponding redox peaks, which clearly reflect the delithiation–lithiation processes. These voltammetric studies show a pronounced difference in the behavior of the electrodes at elevated temperatures. As seen in Fig. 2, upon repeated cycling at 60 °C, the electrode's capacity decreases. It is also very significant that the CVs measured at 60 °C at the slow scanning rate do not exhibit the two redox peaks, as seen in the CVs measured at 25 and 45 °C (not shown here). As the temperature is higher, the electrode's kinetics should be faster, and hence, its CV redox peaks should be sharper with a smaller hysteresis. These voltammetric

measurements clearly demonstrate that increasing the temperature slows the electrodes' kinetics in all the three solutions. Cyclic voltammograms of LiCoO₂ electrodes recorded after prolonged storage show that the higher the temperature of storage, the smaller is the capacity measured in the voltammetric studies. In fact, a prolonged storage of LiCoO₂ electrodes (several weeks) in the above solutions leads to almost featureless voltammetric responses and a pronounced decrease in the voltammetric peak currents (I_p). For instance, Fig. 3a–c present first delithiation–lithiation voltammetric cycles of the LiCoO₂ electrodes measured from OCV (≈ 3 V vs. Li/Li⁺) to 4.25 V at 60 °C at a very slow potential scanning rate ($\nu = 0.01$ mV/s, corresponding to approximately a C/30 rate in galvanostatic cycling) in the three solutions, as indicated. These figures also

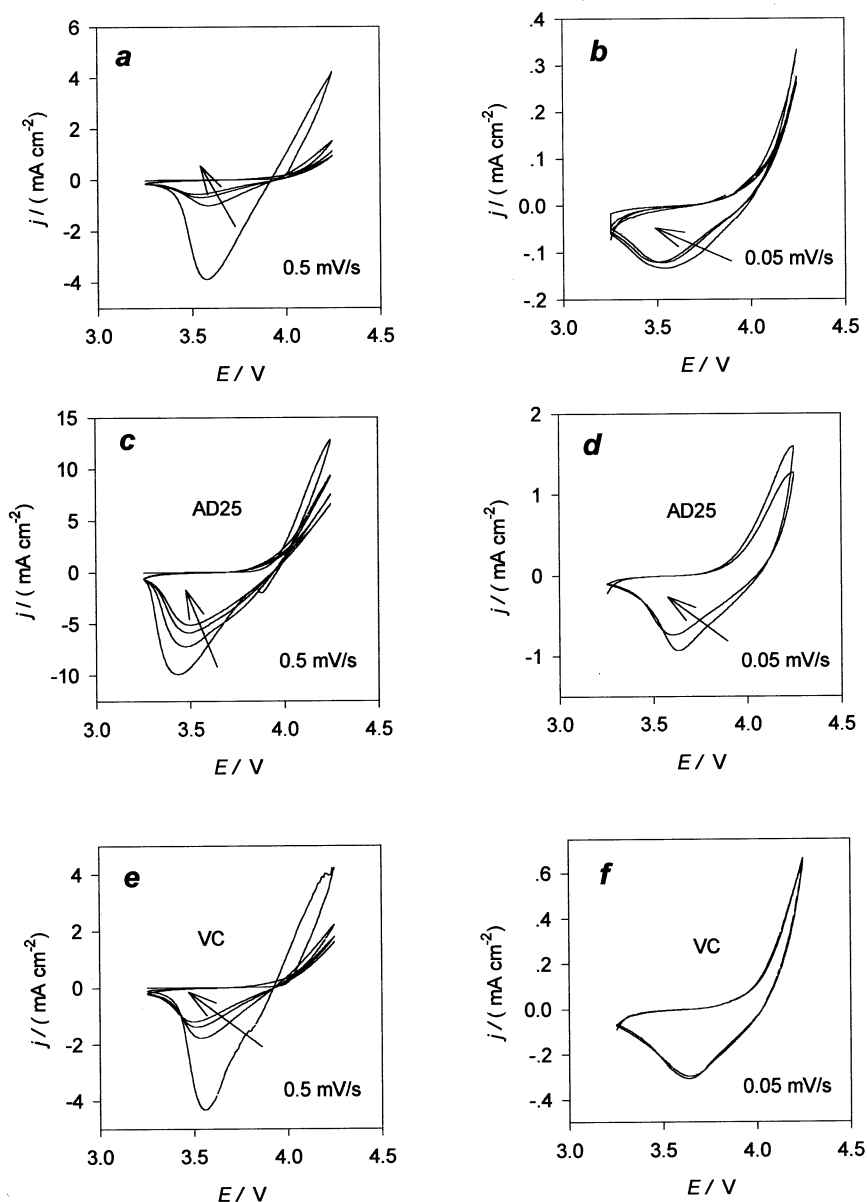


Fig. 2. Same as Fig. 1. Measurements were performed at 60 °C.

present CVs obtained from the same electrodes after storage in the cells for 7 days, as well as the corresponding changes in OCV during storage (insets). These experiments indicate that the LiCoO_2 electrodes have a faster kinetics in an AD25-containing solution, compared with that in standard or VC-containing solutions. From these results, we can conclude that storage at 60 °C leads to the apparent capacity loss of the electrodes, which may result from major structural changes of the active mass, or from more sluggish kinetics. The average capacity loss per day during storage of LiCoO_2 electrodes at constant potential ($E = 3.87$ V) at 60 °C was around 2% for standard and VC-containing solutions, and 0.45% for a solution containing AD25.

Fig. 4 summarizes the voltammetric studies of the LiCoO_2 electrodes in the three solutions at three temperatures: 25, 45, and 60 °C. It compares the dependence of the cathodic peak currents, obtained from the CVs of electrodes at their stable voltammetric behavior, as a function of the square root of the potential scanning rate. For diffusion-controlled reactions, I_p versus $\nu^{-1/2}$ plots should be straight lines. As seen in this figure, the behavior of the electrodes in the three solutions is remarkably different. For the standard solution (no additives), as the temperature is higher, the currents are lower. There is a difference of close to an order of magnitude between the currents measured at 25 and at 60 °C. A similar trend is seen for the voltammetric behavior of the electrodes in the solutions

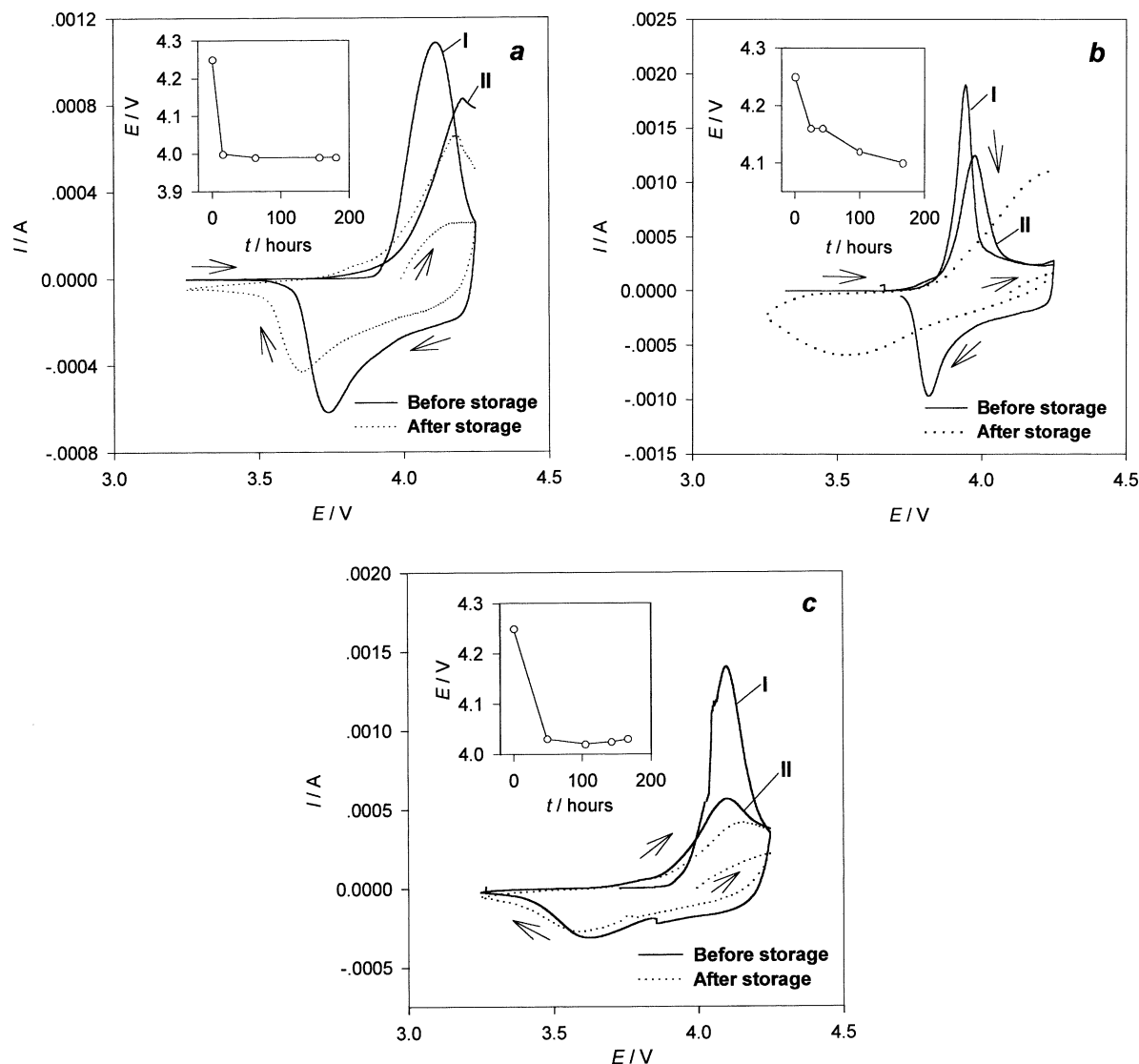


Fig. 3. A comparison of the voltammetric behavior of LiCoO_2 electrodes at 60 °C before and after storage for 7 days in an EC–EMC/ LiPF_6 solution (a), and in solutions containing AD25 (b) and VC (c). The insets show changes in the OCV of the electrodes during storage. First and second cycles are indicated where necessary.

containing VC. However, the effect of the temperatures (lowering the currents measured) is much less pronounced compared with the standard solution. It is important to note that the CV currents measured at 25 °C in the standard solution are higher than those measured in the solutions containing VC. In contrast to both the above cases, the effect of temperature on the CV currents measured in solutions containing AD25 is minimal, and in general, the CV currents measured in these solutions are higher than those recorded with the standard and VC-containing solutions. These results clearly exhibit pronounced interrelations between effect of temperature and the impact of solution composition on the electrochemical behavior of LiCoO_2 electrodes in the EC–EMC/ LiPF_6 solutions.

After cycling and subsequent storage, the cells' solutions were studied by ICP. All solutions measured by ICP after prolonged storage contained a few mg/l of cobalt. These values correspond to a dissolution of only 0.01–0.03% of the total cobalt content of the electrodes. These solutions were also studied by EQCM.

Fig. 5a shows typical first voltammetric cycles measured with pristine (fresh) solutions with nickel electrodes in EQCM experiments at 25 °C. In general, the voltammograms are typical of noble metals electrodes in polar aprotic Li salt solutions [18]. The irreversible cathodic peak around 1.2 V relates to reduction of trace water, salt anion and solvent (this peak does not appear at subsequent cycles) [18]. The cathodic peak around 0.5–0.6 V relates to Li underpotential deposition on

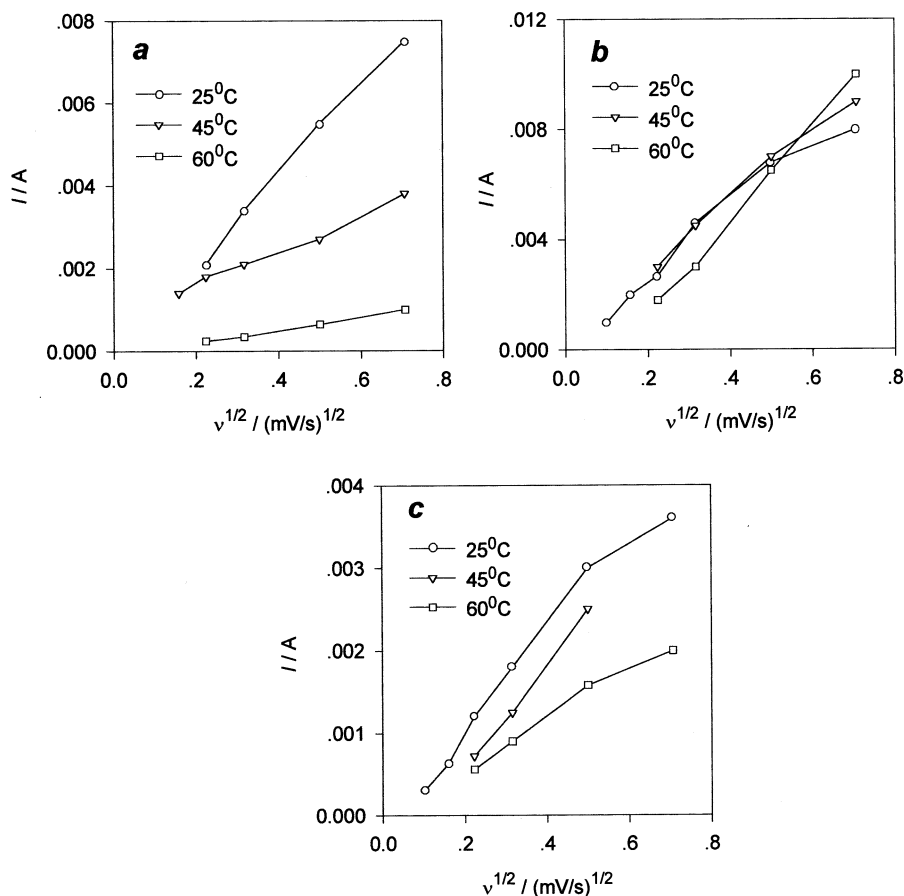


Fig. 4. I vs. $(v)^{1/2}$ plots derived from cyclic voltammetry measurements of LiCoO_2 electrodes in EC–EMC/ LiPF_6 solution (a), and in solutions containing AD25 (b), and VC (c) at 25, 45 and 60 °C.

nickel. The anodic peaks around 1.1 and 1.5 V relate to the stripping of the underpotential deposited Li. The anodic peak between 2.0 and 2.5 V relates to oxidation of adsorbed hydrogen (formed by the cathodic reduction processes) on nickel [18]. It is very significant that when the solutions contain the reactive additives, VC or AD25, the first, irreversible cathodic process (reduction of solution species) starts at higher potentials (onset around 2 V vs. Li/Li^+), but the cathodic currents measured are lower compared with the additive-free solutions. This behavior reflects the passivation of the electrodes, probably due to reduction of the additives that form insoluble surface species.

Fig. 5b shows the mass accumulation on the electrodes in the EQCM experiments, to which the CVs of Fig. 5a belong. As expected from the difference in the currents seen in Fig. 5a, the mass accumulation on the electrode during the first cathodic process in the additive-free solution was the highest. The mass per electron (m.p.e.) values for these processes described in Fig. 5a and b, which range between 10 and 20 g/mol, are much lower than the equivalent weight of the typical inorganic and organic species (salts and oxides, e.g. ROCO_2Li , ROLi , Li_2CO_3 , LiOH , Li_2O , LiF) that

precipitate on noble metal and carbon electrodes at low potentials or on Li electrodes in these solutions [19]. As already discussed and explained, these low m.p.e. values reflect the formation of surface films that partially dissolve in the solutions (in the EQCM experiments there is an excess of solution in the cells) [19].

Fig. 6a–d show the results of EQCM experiments with solutions from LiCoO_2/Li cells in which LiCoO_2 electrodes were cycled and then stored. All four presentations of these figures include CV and mass versus E response in first cycle experiments with Ni electrodes. The processes of constant m.p.e. values are marked in the mass vs. E curves and the relevant m.p.e. values are indicated. Fig. 6a–c, which relate to additive-free, VC- and AD25-containing solutions, reflect similar pronounced cathodic processes at potentials between 1.5 and 1.0 V (Li/Li^+), and mass accumulation processes at potentials lower than 2.0 V (Li/Li^+) with constant m.p.e. values around 30 g/mol. Fig. 6d shows similar results for a pristine, additive-free solution containing 1000 ppm of Co^{+2} (cobalt salt). As seen in Fig. 6d, the cathodic process of a Ni electrode with this solution is also characterized by a mass accumulation with m.p.e. close to 30 g/mol. We attribute the cathodic processes

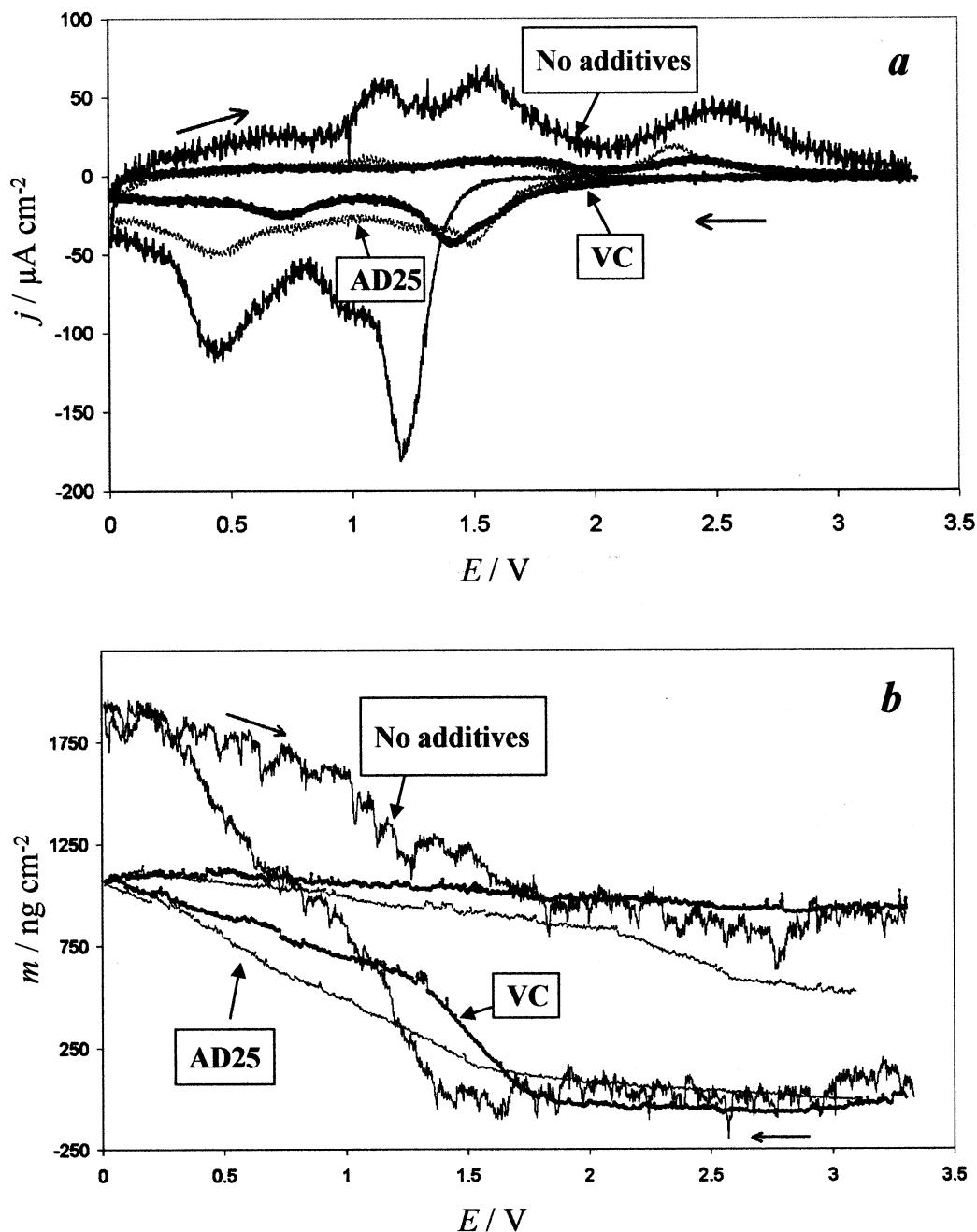


Fig. 5. (a) Cyclic voltammograms obtained at 25 °C in EQCM experiments from Ni/Li cells in EC–EMC/LiPF₆ solution and in solutions containing AD25 and VC, as indicated. Potential scan rate was 5 mV/s. (b) Mass accumulation changes corresponding to the EQCM experiments of (a).

with m.p.e. close to 30 g/mol, seen in Fig. 6a–d, to cobalt deposition, namely, $\text{Co}^{+2} + 2\text{e}^- \rightarrow \text{Co}$, where the atomic weight of cobalt is ≈ 59 , and therefore the expected m.p.e. is indeed ≈ 30 g/mol. The Li counter electrodes from the EQCM experiments were analyzed by XPS, and they did indeed show distinctive Co peaks at binding energies around 784 and 800 eV (corresponding to metallic cobalt and cobalt oxide, respectively) [20].

Hence, the EQCM experiments and related XPS measurements converge with the ICP measurements and clearly show that cobalt dissolves from the LiCoO₂ cathodes to the solutions upon cycling and/or prolonged storage, and may be deposited as metallic cobalt on the anodes. Li anodes from cycling/storage experiments of Li/LiCoO₂ cells with all the three solutions at 25, 45, and 60 °C were analyzed by XPS with special emphasis on the detection of cobalt on the surfaces of the Li anodes.

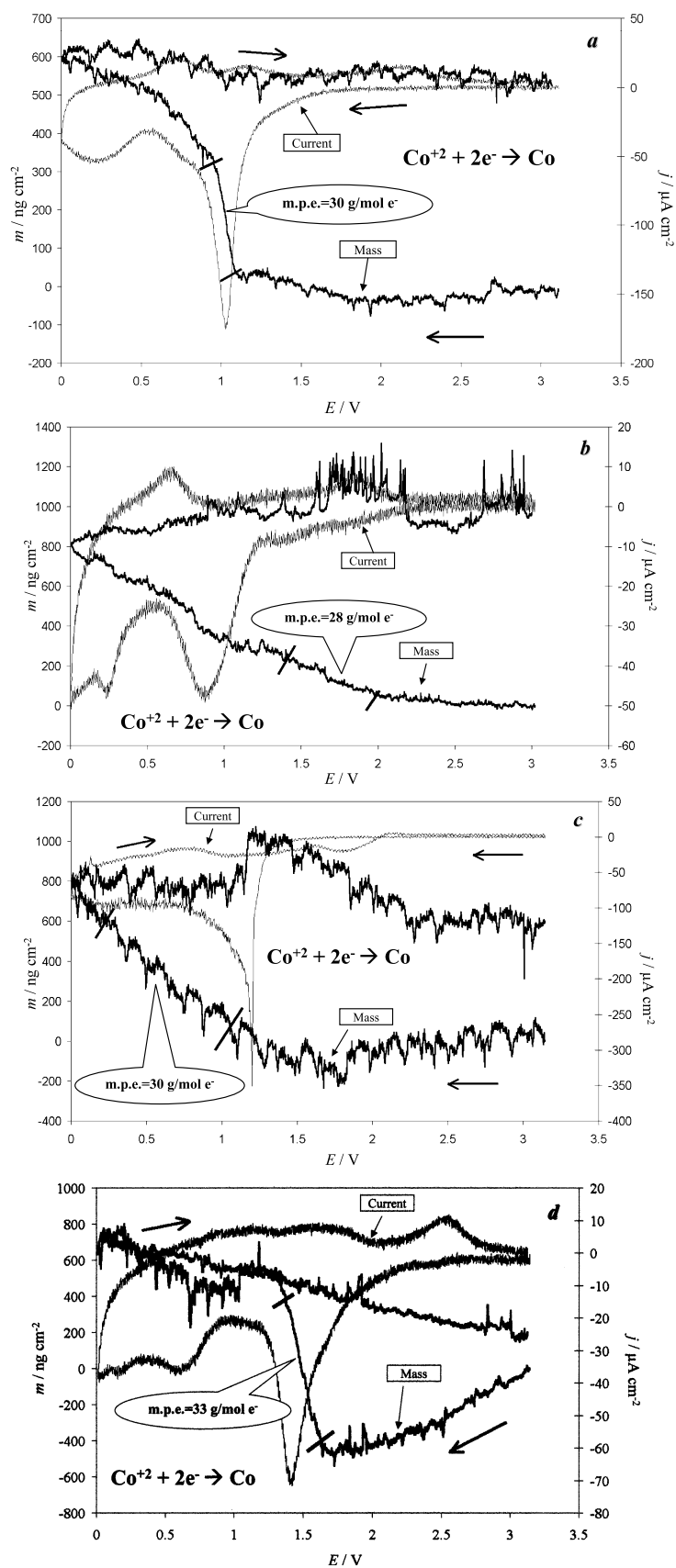


Fig. 6

Fig. 7 shows typical XPS data from Li electrodes taken from Li–LiCoO₂ cells after cycling/storage. Two examples are presented. Fig. 7a belongs to a Li electrode

from a cell cycled with a solution containing AD25 at 60 °C, and Fig. 7b belongs to a similar experiment with a solution containing VC (60 °C). The data include

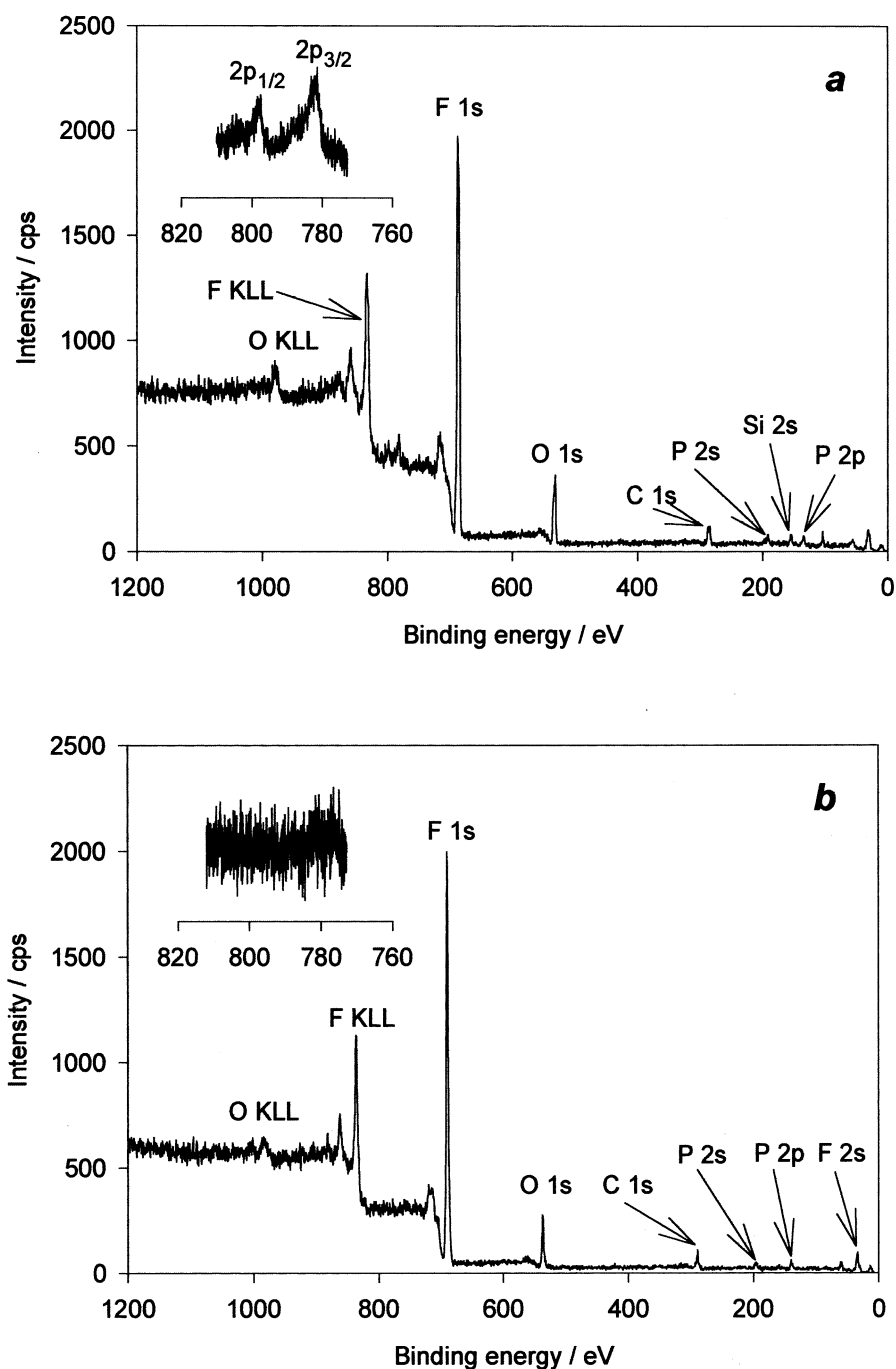


Fig. 7. XPS data obtained from lithium counter electrodes of cycled and stored Li–LiCoO₂ cells: (a) an EC–EMC/LiPF₆ solution containing VC (60 °C, 32 days); (b) an EC–EMC/LiPF₆ solution containing AD25 (60 °C, 32 days). The region where cobalt peaks appear is enlarged in the upper

Fig. 6. (a) Cyclic voltammograms (5 mV/s) and mass accumulation changes obtained in EQCM experiments (25 °C) from Ni/Li EQCM cells loaded in an EC–EMC/LiPF₆ solution, collected from Li–LiCoO₂ cells after cycling and storage at 25 °C. (b) Same as (a). The EC–EMC/LiPF₆+VC solution was collected from the Li–LiCoO₂ cell after cycling at 25 °C. (c) Same as (a) and (b). An EC–EMC/LiPF₆+AD25 solution. (d) Same as (a)–(c). A Ni/Li EQCM cell. An EC–EMC/LiPF₆ solution, which contains 1000 ppm Co⁺².

spectra of all the relevant elements (marked) with the Co region enlarged (upper, left hand corners). In the case of AD25, no Co could be detected, while in the latter case (VC), cobalt peaks are clearly seen.

The results of these experiments are very significant. Cobalt was not found on the Li anodes in experiments carried out at 25 °C. With additive-free solutions and solutions containing VC, cobalt was found on the Li anodes only after cycling and storage experiments carried out at 45 or 60 °C. When the solutions contained AD25, no cobalt could be detected on the Li electrodes, no matter what the temperature of the cycling/storage experiments was. However, it is clear from the ICP measurements and the EQCM experiments that cobalt dissolves from the cathodes to the solutions at 25 °C as well, even when the solution contains AD25. Therefore, the above results reflect the passivation status of the Li anodes as a function of the temperature and the presence of additives. It appears that only at elevated temperatures do the surface films formed on the Li anodes allow Co deposition, and when the solutions contain AD25, the passivation is efficient and therefore avoids Co deposition, even at elevated temperatures.

The fact that Co dissolves from the LiCoO₂ cathodes may indicate that, upon cycling or storage of these electrodes, their structure changes, and these changes may be the reason for the decrease in the apparent electrode capacity fading observed due to cycling or storage, as demonstrated in Figs. 1–4 that present voltammetric studies.

Fig. 8 shows typical XRD patterns of cathodes after cycling and storage experiments at different temperatures, compared with XRD patterns of a pristine

LiCoO₂ cathode. A rigorous comparison between XRD patterns of pristine electrodes and XRD patterns of cycled and stored electrodes at 25–60 °C did not reveal any difference. Both the intensities of the diffraction peaks (the main ones related to 003 and 104 reflections) and their positions are nearly the same. Hence, we conclude that the Co dissolution discussed above only has a negligible, if any, effect on the bulk structural status of the electrodes' active mass. It appears that the LiCoO₂ electrodes are stable when cycled in the 3.25–4.25 V range at temperatures as high as 60 °C. We therefore have to conclude that the apparent capacity loss upon cycling or storage is not due to structural changes, but rather due to surface phenomena on the LiCoO₂ electrodes.

Fig. 9a–c show impedance spectra (Nyquist plots) of LiCoO₂ electrodes measured at $E = 3.87$ V in the three solutions at 25, 45 and 60 °C. In general, these impedance spectra exhibit a small, high frequency semicircle that should be attributed to the resistance of surface films that cover LiCoO₂ electrodes in these solutions, and a medium-to-low frequency big semicircle, which should be attributed to charge transfer resistance (potential dependent), as discussed in our previous publications [21,22]. These impedance spectra demonstrate pronounced temperature and solution composition effects, which correlate with the effects of these parameters on the voltammetric behavior of LiCoO₂ electrodes, as was discussed above. The spectra related to the additive-free solution show a pronounced increase in the high frequency semicircle as the temperature increases from 25 to 60 °C. Note that in this case the low frequency semicircle decreases as the temperature increases from 25 to 45 °C. This result

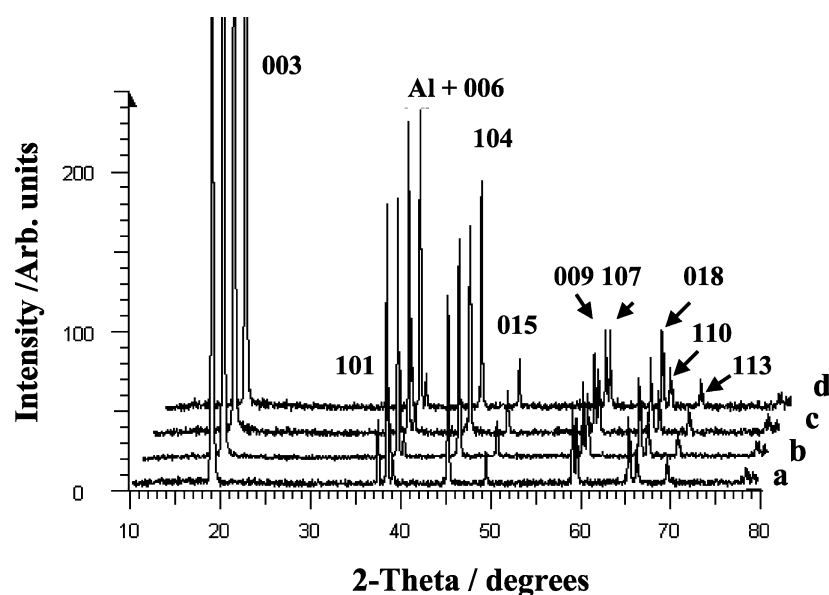


Fig. 8. XRD patterns of LiCoO₂ electrodes: (a) pristine (as-prepared at LG Chem.); (b) stored at OCV (60 °C, 20 days) in EC–EMC/LiPF₆ solution; (c) and (d) cycled and stored in EC–EMC/LiPF₆ solution at 45 (40 days) and 60 °C (32 days), respectively.

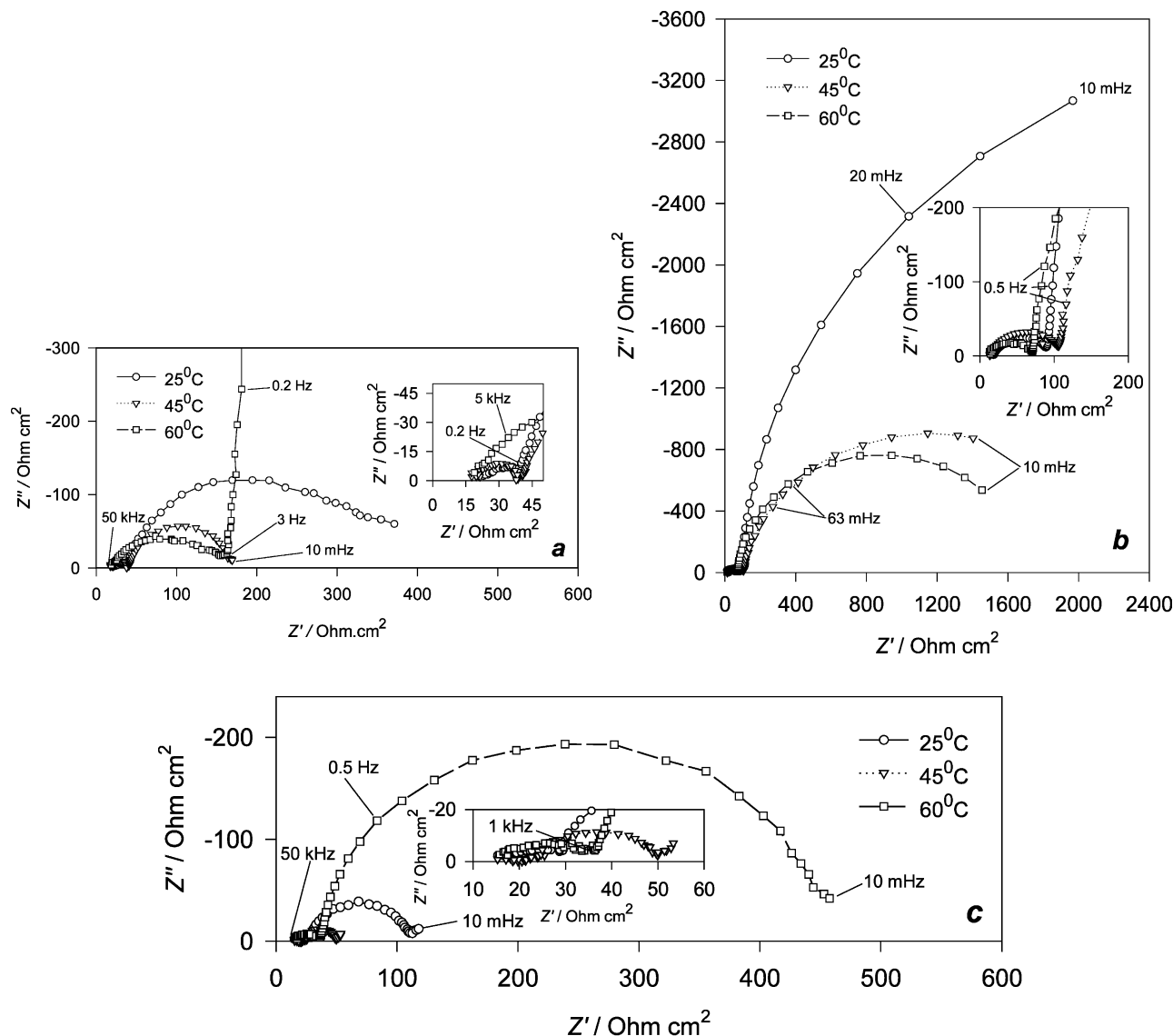


Fig. 9. Electrochemical impedance spectra measured from LiCoO_2 electrodes at OCV $E = 3.87$ V on the anodic wave (delithiation) of the cyclic voltammogram. Prior to impedance measurements, the electrodes were stabilized (several CVs at gradually decreasing scanning rates) at 25, 45 and 60 °C in a mother EC-EMC/ LiPF_6 solution (a), and solutions containing VC (b) and AD25 (c).

shows that a 20 °C increase in the temperature, decreases as expected, the charge transfer resistance. However, when the temperature increases further by 15 °C from 45 to 60 °C, the surface of the electrodes changes so that their impedance increases considerably. In the case of the VC-containing solution, the electrodes' impedance is higher than that measured in the standard (additive-free) solution at 25 and 45 °C, but much lower in the presence of VC at 60 °C compared with that in the additive-free solution. The impedance measured in the solutions containing AD25 decreases as the temperature increased from 25 to 45 °C. At 60 °C, the impedance measured in solutions containing the AD25 additive is considerably higher than that measured at lower temperatures. However, it is much lower com-

pared with the impedance measured at 60 °C in the standard or VC-containing solutions. These EIS measurements clearly show that the LiCoO_2 electrode surfaces differ considerably in the three solutions, and demonstrate the strong effect of temperature on the state of the surfaces of the electrodes.

Fig. 10 shows impedance spectra of LiCoO_2 electrodes measured at $E = 3.87$ V (Li/Li^+) in the standard solution during prolonged storage at 25 °C. As expected, the impedance of the electrodes increases upon storage. This trend is common to these electrodes in all the three solutions and temperatures (25, 45, and 60 °C) after cycling or during storage. It is clear from these experiments that upon storage, there are gradual, continuous changes at the electrodes' surfaces (thicken-

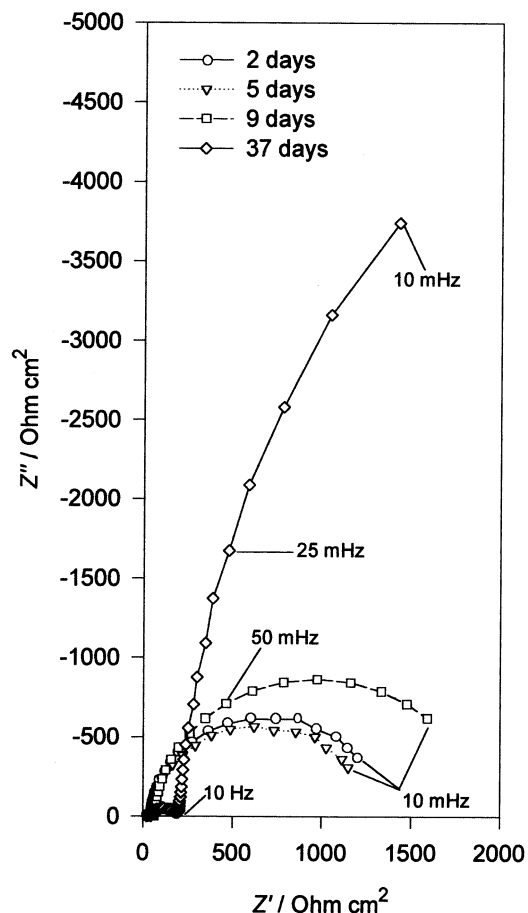


Fig. 10. Electrochemical impedance spectra measured from LiCoO_2 electrodes at OCV $E = 3.87$ V on the anodic wave (delithiation) of the cyclic voltammogram. The electrodes were cycled and stored at 25°C in the EC–EMC/ LiPF_6 solution. Storage time is indicated.

ing of the surface films and/or their rearrangement), which increase their impedance.

The impedance measurements described above seem to indicate that the LiCoO_2 electrodes develop in the three solutions surface films that contribute to their surface resistance. The fact that the electrodes' surface resistance increases with temperature and with storage time at OCV conditions, means that these surface films are not stable, but rather involve dynamic processes during storage at OCV.

Fig. 11 shows FTIR spectra (diffuse reflectance mode) of powders scraped from a pristine LiCoO_2 electrode, from an electrode stored at $E = 3.87$ V at 60°C , and from an electrode cycled and stored at 25°C (a–c, respectively). The spectra of a pristine electrode and electrodes stored at a discharged state (no cycling) are very similar and contain some peaks around 700, 850, 900, 1200, 1300, and 1400 cm^{-1} , which may be attributed to absorption bands of the binder (PVdF) [23]. The spectrum of the cycled and stored electrode is quite different and contains many inverse peaks around 1800, 1490, 1400, 1150, 1080, 870, 840, and 770 cm^{-1} ,

which may be attributed to polycarbonate species, polymerization products of EC [24]. It is well known that monolayers of species adsorbed to electrically insulating surfaces often show inverse FTIR peaks in the absorbance mode [25].

Figs. 12 and 13 show FTIR spectra measured from electrodes cycled and stored at 25 and 60°C in solutions containing AD25 and in solutions containing VC (respectively). The two spectra related to the solutions containing AD25 (Fig. 12a and b, 25 and 60°C , respectively), are similar but not identical to Fig. 11, spectrum c. Both spectra include inverse peaks that could be attributed to a monolayer of polycarbonate (probably poly-EC) on the insulating LiCoO_2 's electrode active mass. However, there are slight changes between spectra related to additive-free solutions and solutions containing AD25, especially in the finger print region between 800 and 1200 cm^{-1} . In this region, the inverse peaks are superimposed on normal absorbance bands (going upwards), which probably relate to a multilayer surface film. The resolution of spectra obtained in the diffuse reflectance mode (DRIFT) is usually low, and very rarely allows a rigorous identification of surface species unless the spectra obtained by DRIFT can be compared with a well prepared library of relevant reference spectra (obtained by transmittance or reflectance modes). However, these spectral studies using DRIFT are useful for obtaining general information about the state of electrodes' surfaces, and for comparison with similar surfaces that underwent different surface processes. In this respect, a comparison between the spectra related to additive-free and AD25-containing solutions suggest that the presence of AD25 in solutions indeed influences the electrodes' surface chemistry and enriches the surface of the active mass by, as yet unidentified, surface species that are not formed in the reference solutions. Fig. 13, spectra a and b, related to VC-containing solutions in experiments at 25 and 60°C , are different from Fig. 11, spectra c, Fig. 12, spectra a, and b, as they are characterized by IR peaks going upwards, which are typical of surface species deposited on insulating substrates in multilayers. In Fig. 13b, all the IR bands go upwards, and include peaks around 1800, 1780, $1480\text{--}1320$, 1170, $1080\text{--}1050$, and $950\text{--}900\text{ cm}^{-1}$, all of which can be attributed to polycarbonates [24]. Indeed, VC, which has a $\text{C}=\text{C}$ double bond, is the most likely of all the other solution components (alkyl-carbonate solvents, AD25 etc.) to undergo polymerization. VC polymerization can be easily induced at both high and low potentials (cationic vs. anionic polymerization). We should add to these spectral data some information obtained by XPS measurements: qualitatively speaking, LiCoO_2 powder stored in LiPF_6 /alkyl-carbonate solutions always shows LiF peaks. However, a quantitative-comparative

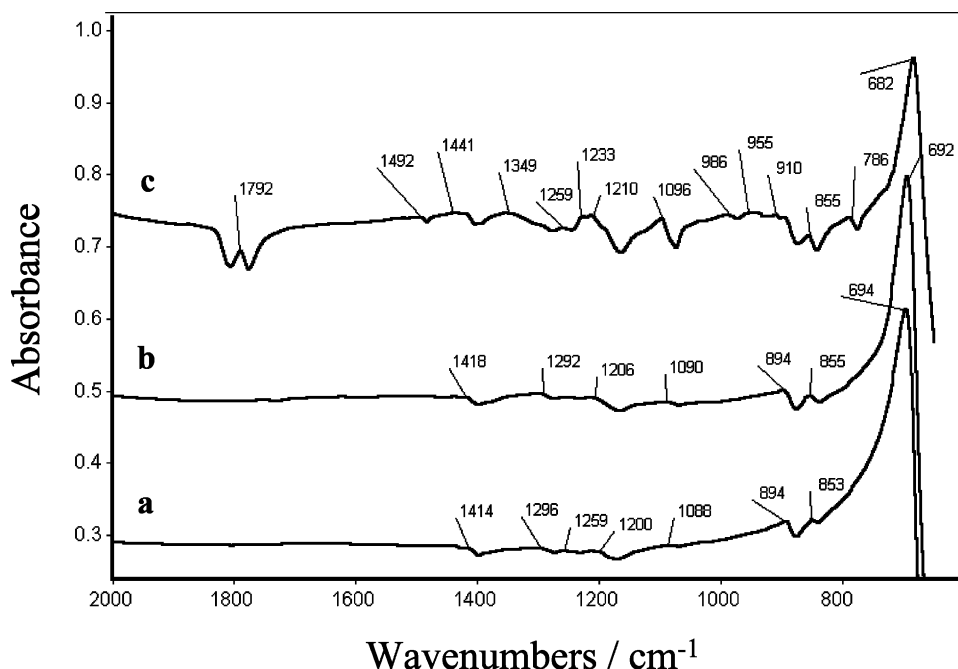


Fig. 11. FTIR spectra (diffuse reflectance mode) obtained from LiCoO_2 electrodes: (a) pristine; (b) stored (20 days, 60 °C) at OCV $E = 3.87$ V in an EC–EMC/ LiPF_6 solution; (c) cycled at C/10 rate in a sandwich-type cell and subsequently stored (30 days, 25 °C) in an EC–EMC/ LiPF_6 solution.

analysis of LiCoO_2 powders stored at different conditions is not reliable. Hence, the organic surface films detected by FTIR spectroscopy are always accompanied by the formation of surface LiF (formed by acid–base reactions between HF and LiCoO_2). It is well known that LiF films are highly resistive for Li-ion migration. Thus, the formation of organic surface species may suppress the formation of LiF on the cathodes' surfaces.

Although we did not check the effect of the LiCoO_2 electrode's potential on storage (in terms of impedance and surface chemistry), from the difference in FTIR spectra of electrodes stored at 3.87 V and of electrodes cycled (see Fig. 11b and c), we suggest that as the potential is higher, formation of organic films is more favorable, due to possible polymerization of EC (or VC) via cationic mechanisms.

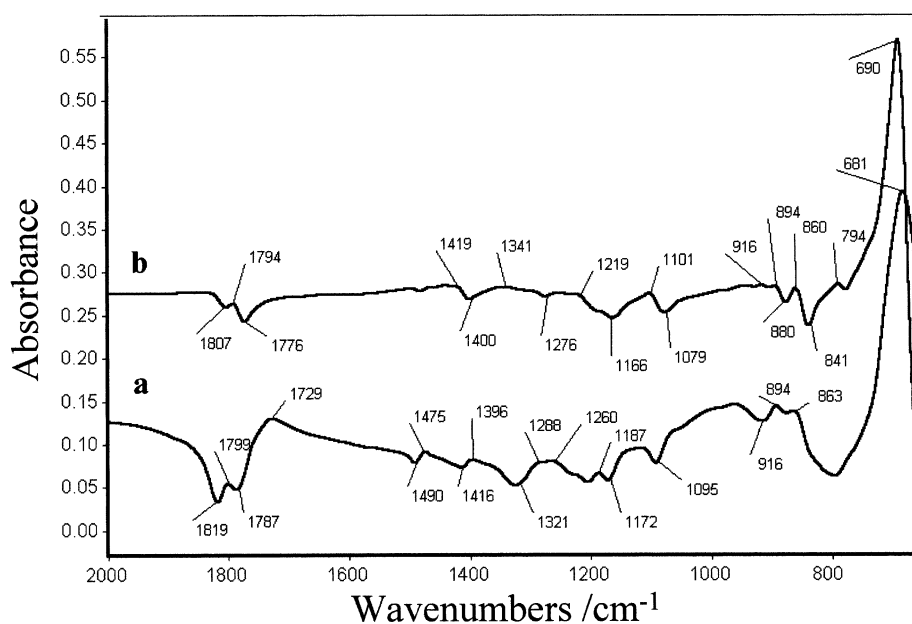


Fig. 12. Same as Fig. 11. LiCoO_2 electrodes were cycled and stored in an AD25-containing solution at 25 °C for 25 days (a), and at 60 °C for 32 days (b).

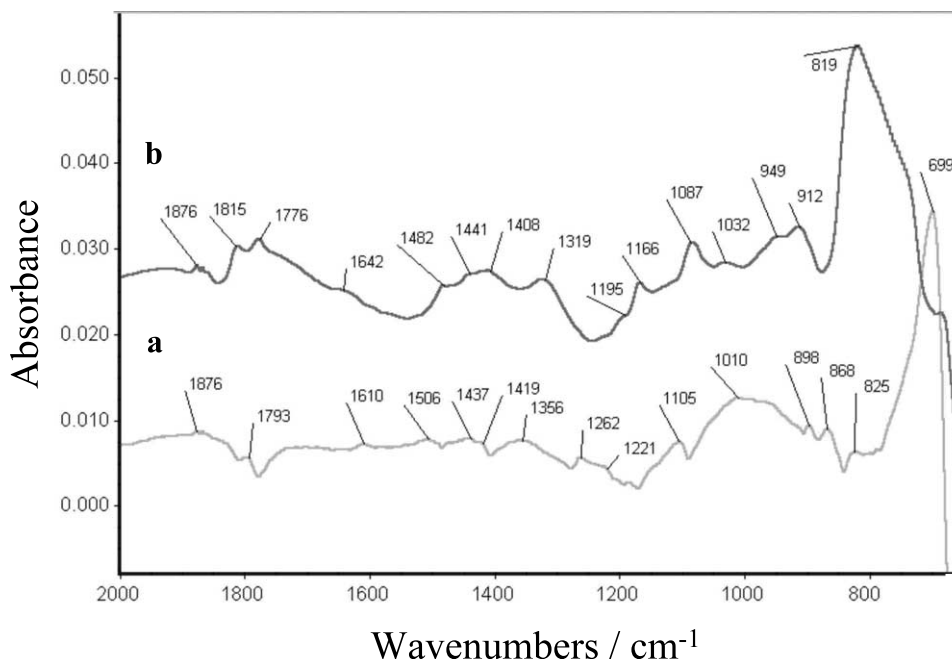


Fig. 13. Same as Fig. 12. LiCoO₂ electrodes were cycled and stored for 32 days in VC-containing solution at 25 (a) and at 60 °C (b).

The impedance, IR and XPS measurements described above converge to the following picture: EC, VC, and probably AD25, polymerize on the cathode surfaces, and this possible polymerization is more favorable as the temperature is higher and it intensifies during prolonged storage. In parallel, acid–base reactions between trace HF and LiCoO₂ form surface LiF. The latter surface species may form highly resistive films. We may attribute the increase in the electrode's impedance at elevated temperatures and prolonged storage in any LiPF₆ solution mostly, to the intensive formation of LiF. LiF formation is suppressed in VC- or AD25-containing solutions due to the competitive reactions of these additives on the electrode surfaces. Thus, the electrodes' impedance in the presence of these additives, especially at elevated temperatures, may be lower than that measured in the reference, additive-free solutions. However, at elevated temperatures the surface reaction of the additives also intensifies, and thus, the electrodes' impedance increases in temperature due to the formation of polymeric organic films (e.g. poly-vinylencarbonate).

Fig. 14 presents results of morphological studies of LiCoO₂ electrodes by SEM. Fig. 14a shows a pristine electrode comprising micron size LiCoO₂ particles of 8–10 μm in diameter embedded in the polymeric matrix that also contain submicronic, carbon black particles. Fig. 14b shows a SEM micrograph of an electrode that was cycled and stored at 60 °C in an additive-free solution. Fig. 14c shows an electrode that was cycled and stored for 30 days in a solution containing AD25 (25 °C), whose impedance was usually an order of magnitude higher than that of a pristine electrode.

Visible changes can be seen in this micrograph, compared with the micrograph of the pristine electrode. Surface films cover all the particles of the LiCoO₂ electrode cycled and stored in the AD25-containing solution. Similar conclusions emerge when comparing micrograph 14d related to an electrode stored at 60 °C in a VC-containing solution to the pictures of pristine electrodes. Although the electrode's morphological changes in Fig. 14d compared with those seen in Fig. 14a are not as drastic as the changes seen for the electrode after prolonged storage in EC, EMC/LiPF₆+AD25 solution (Fig. 14c), it is clear that the treatment in the VC-containing solution also leads to the formation of surface films that cover the LiCoO₂ particles (Fig. 14, micrograph d). In general, SEM micrographs of cycled and stored electrodes in all the solutions at 25–60 °C show morphological changes that can be attributed to the formation of surface films on the electrodes.

4. Conclusion

LiCoO₂ electrodes stored in an excess of LiPF₆ solutions or cycled at elevated temperatures show an apparent deterioration in their performance. When cycled at similar rates, practical LiCoO₂ electrodes stored at elevated temperatures, and even at room temperature for prolonged periods (weeks), show apparent capacity fading. Analysis of the solutions revealed that cobalt dissolves in the solutions and can be deposited as metallic cobalt on the counter electrodes (Li or Li–C anodes). However, it appears that the deterioration in performance upon storage and/or

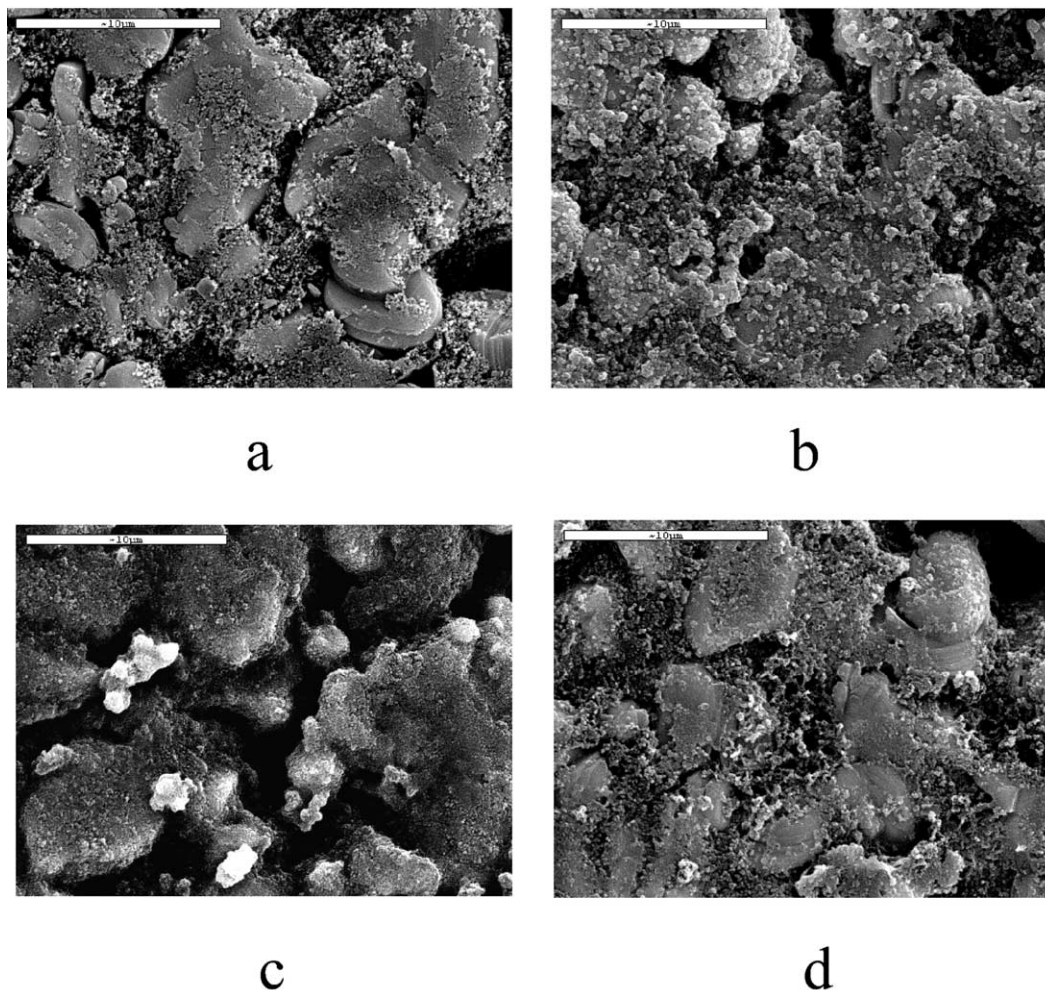


Fig. 14. SEM micrographs of the LiCoO_2 electrodes: (a) a pristine electrode; (b) an electrode cycled and stored at 60 °C, 32 days in an EC–EMC/ LiPF_6 solution; (c) an electrode cycled and stored at 25 °C, 30 days in an AD25-containing solution; (d) an electrode cycled and stored at 60 °C, 32 days in a VC-containing solution.

charge–discharge cycling at elevated temperatures that may appear as a capacity fading, is not because of bulk changes of the LiCoO_2 active mass, but rather relates to surface phenomena. LiCoO_2 electrodes develop surface films in LiPF_6 /alkyl-carbonate solutions. These films contain LiF , which is the product of the acid–base reaction between LiCoO_2 and trace HF unavoidably present in LiPF_6 solutions. The films also contain organic species. These may include ROCO_2Li species, which are products of possible nucleophilic reactions between LiCoO_2 and alkyl-carbonate molecules that are electrophiles [26]. The FTIR spectral studies provide evidence that polycarbonate species are also formed on the electrodes. EC may be polymerized on the cathodes by cationic mechanisms. Precipitation of surface films on the cathodes, which intensifies at elevated temperature and/or during prolonged storage (even at room temperature), increases the electrode's impedance. It is known that LiF films are very resistive to Li-ion migration through them. Surface film formation may

also interfere badly with the interparticle electrical contact, and hence, adds internal impedance and problems of electrical contact between the active mass and the current collector. Hence, the apparent capacity fading observed for LiCoO_2 electrodes during cycling at elevated temperatures and prolonged storage is due to an increase in the electrodes' impedance. The surface chemistry of the LiCoO_2 cathodes can be largely attenuated by the presence of additives that can react on the electrodes' surfaces (e.g. polymerization), and form stable and steady surface films. This was demonstrated in the present work using VC or an organo-borate complex (Merck's AD25). Using the latter additive, the apparent capacity of the electrodes is retained at 60 °C because their kinetics do not deteriorate when cycled and stored at elevated temperatures. It was interesting to find that in spite of the fact that cobalt always dissolves from the cathodes into the solutions, and cobalt ions are reduced on the Li or Li–C anodes to metallic cobalt, in the presence of the organo-borate

complex, there is no cobalt deposition on the anodes (in contrast to cases of additive-free or VC-containing solutions in which cobalt is deposited on the anodes). This finding shows that the presence of this organo-borate complex in solutions has a very positive impact on the passivation of the anodes (Li, Li–C), as is indeed known from previous studies [27].

It should be noted that the effect of additives depends very strongly on the solutions' composition. We currently find that the impact of additives such as VC, organo-borate complexes or silanes, strongly depends on both the salts and the solvent mixtures used in Li-ion battery systems.

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