

Electrode–solution interactions in Li-ion batteries: a short summary and new insights

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Abstract

This paper is aimed at reviewing and discussing several selected surface phenomena related to Li-ion batteries. Accumulated data from in situ XRD, in situ AFM, SEM, and electrochemical measurements of graphite electrodes comprising different types of graphite particles (in terms of morphology and 3D structure) converge to a description of failure mechanisms of graphite electrodes, which involve deactivation by insulating surface films that surround cracked particles. It appears that the performance of the cathodes is also, to a large extent, surface film controlled. Hence, aging of Li-ion batteries relates mostly to surface phenomena that increase the electrodes' impedance, especially at elevated temperatures. Attempts to improve the performance of Li-ion battery systems by introduction of new salts and reactive additives are reviewed. The impact of elevated temperatures (up to 80 °C) is also discussed.

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1. Introduction

The apparent stability and good performance of the lithiated carbon anodes and the transition metal cathodes of Li-ion batteries in the commonly used electrolyte solutions (mixture of alkyl carbonate solvents and a Li salt) is due to complicated electrode–solution interactions and passivation phenomena. The first replacement to Li metal anodes for rechargeable battery systems was graphite. Over the years, the correlation among the surface chemistry, morphology, 3D structure, and the electrochemical behavior of graphite electrodes in Li battery electrolyte solutions has been intensively investigated [1]. Polarization of graphite electrodes, as well as polarization of any metallic electrode in a non-aqueous Li salt solution, forms surface films on the electrodes, which are insoluble Li salts, products of reduction of solution species [2]. Since the structure of graphitic carbons is so fragile, graphite electrodes can be easily destroyed or deactivated due to side reactions and cointercalation of other solution species with Li-ions, which leads to exfoliation of the graphene planes [3]. Hence, the stability of lithiated graphite electrodes depends on a passivation by protective surface films whose structure depends mostly on the composition of the electrolyte solutions [4]. Since graphitic carbons remain the most important anode materials

for Li-ion batteries, a great deal of effort is invested in the stabilization of graphite electrodes, either by surface treatments [5] or by the use of reactive, filming additives in solutions [6,7]. The cathode side in Li-ion batteries is also very interesting in relation to electrode–solution interactions. The oxidation of Li-ion battery solutions was investigated in recent years [8]. However, the question as to whether alkyl carbonate solvents are oxidized by the high voltage cathode materials (delithiated Li_xMO_y , $E > 4\text{ V}$ versus Li/Li^+) remains open.

It is now generally accepted that the commonly used cathodes (e.g. LiMn_2O_4 , LiNiO_2 , LiCoO_2) are also covered by surface films that are formed spontaneously by solution–cathode surface reactions [9].

Critical subjects that are highly important to the field of Li-ion batteries relate to the capacity-fading mechanisms of the various electrodes, especially at elevated temperatures and aging processes of Li-ion batteries. These subjects were also investigated intensively in recent years [10].

This paper reviews selected interesting surface phenomena in Li-ion batteries, and is aimed at answering the following questions:

1. How and why do graphite electrodes fail?
2. How do electrolyte solutions interact with cathode materials?
3. What are the aging scenarios of Li-ion batteries, especially at elevated temperatures?

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4. How the performance of Li-ion batteries can be improved by a good selection of salts and additives?

Due to volume limitations, the paper discusses and reviews mostly experimental results coming from the author's group. This should provide the readers with a concise summary of some major conclusions obtained from our recent studies.

2. Experimental

In general, synthetic graphite flakes were obtained from Timrex Inc. Cathode materials, as well as Li battery grade, ready to use electrolyte solutions of all kinds, were obtained from Merck KGaA. Bicarbonates and pyrocarbonates were synthesized and purified in-house. We used two types of thin layer electrochemical cells: T-type and coin-type cells (based on standard 2030 cells from NRC, Canada) that contain Li reference electrodes. The composite anodes usually include synthetic graphite flakes (Timrex Inc.), PVdF binder (5–10%), and copper foil current collectors. The composite cathodes usually include lithiated cobalt oxide or lithiated manganese oxide (spinel) from Merck KGaA, conductive carbon black (10%), PVdF binder (5%), and aluminum foil current collectors. The electroanalytical characterization included a simultaneous use of PITT, slow scan rate CV and impedance spectroscopy, in addition to chronopotentiometry and fast scan rate voltammetry [11,12]. The characterization of the electrodes' surface included FTIR, XPS [13], in situ AFM [14], and SEM. The 3D structure was determined by in situ and ex situ XRD [15]. Electrochemical measurements were carried out at five selected temperatures: 25, 30, 45, 60, and 80 °C.

3. Results and discussion

3.1. Carbon electrodes

It was clearly demonstrated that graphite, hard and soft disordered carbons, and carbon nanotube electrodes develop a similar surface chemistry in the same solutions [16]. When the solutions do not contain HF (e.g. LiClO₄, LiAsF₆, LiN(SO₂CF₃)₂, LiN(SO₂CF₂CF₃)₂ solutions), the surface chemistry is dominated by solvent reduction. Hence, in alkyl carbonate solutions, the major surface species formed are R(OCO₂Li)₂ (reduction products of EC, PC), ROCO₂Li and ROLi (reduction products of DMC, EMC, etc.), and Li₂CO₃ (a reaction product of trace H₂O with ROCO₂Li.) [13]. At a high HF content (e.g. in LiPF₆ solutions, at high solution volume/electrode mass ratios and conditions for hydrolysis) the surface chemistry is dominated by LiF and ROLi. (ROCO₂Li are removed from the surface due to their reaction with HF.) The carbon particles used as anode materials, initially have oxygen-containing surface groups

(easily detected by FTIR and XPS [13]), including OH, COOH, C=O, etc. which are also reduced to –OLi, –COOLi, etc. during a first cathodic polarization. However, what dominates the surface chemistry of the carbons is obviously the reduction of solution species, which produces multilayer surface films (while reduction of the surface groups on the carbon produce no more than a monolayer of Li-containing groups).

In a number of electrolyte solutions including ethers, esters, some linear alkyl carbonates (DMC, DEC) and PC, graphite electrodes fail to insert Li reversibly. The major explanation suggested for the failure of graphite electrodes is: poor passivation → cointercalation of solvent molecules with Li-ion → exfoliation of graphene planes, or deactivation due to reduction of solvent molecules at the edge planes between graphene planes in a way that blocks Li-ion transport inside the graphite [1,3]. We found such a mechanism to be correct for ether solutions [13], but in PC solutions the failure mechanism of graphite electrodes is different. We generally find a strong impact of the morphology and 3D structure (i.e. degree of disorder) of the graphite particles on the behavior of graphite electrodes in PC solutions. Such an impact can not be explained if the failure mechanism involves cointercalation of solvent molecules. In addition, the reversible behavior of Li–graphite electrodes in solutions of EC, which is so similar to PC in many aspects, is striking. Furthermore, in situ AFM imaging of composite graphite electrodes polarized cathodically in PC solutions clearly showed that graphite electrodes do not exfoliate in these conditions. Another important fact is that deactivated graphite electrodes show XRD patterns of graphite, similar to those of the pristine material. Our understanding is, that in PC solutions, internal pressure is developed when PC is reduced within crevices in the edge planes of the graphite particles to R(OCO₂Li)₂ and propylene gas. The particles are cracked, and their fresh reactive surface is exposed and reacts further with solution species. This scenario forms particles covered by electrically insulating surface films, which become deactivated.

Deactivation of graphite particles by surface films that disconnect them electrically from the bulk electrode is a major capacity-fading mechanism of graphite electrodes in all relevant electrolyte solutions, upon prolonged cycling, especially at elevated temperatures. In addition, upon prolonged cycling the graphite electrodes' impedance increases because small scale surface reactions with solution species are inevitable.

Hence, a clear conclusion to be derived from the above discussion is that the performance of graphite electrodes can be improved by improving the properties of their surface films in such a way as to increase their cohesion and elasticity.

The presence of HF, which removes the ROCO₂Li species from the surface due to acid–base reactions that exchange them by LiF, is detrimental. We found that even in LiPF₆ solutions that usually contain HF, elimination of the impact

of contaminants by operating cells with a very high electrode mass/solution volume (e.g. in coin-type cells) enabled us to obtain a very high cycling efficiency with graphite electrodes, even at 80 °C.

3.2. On the cathodes

It was discovered that the Li_xMO_y cathodes (M: Co, Mn, Ni, and binary or ternary mixtures of transition metals) also develop complicated surface chemistry that controls their behavior [2,9].

Fig. 1 compares FTIR spectra of pristine and cycled LiNiO_2 , LiCoO_2 , and LiMn_2O_4 electrodes, as indicated. (Diffuse reflectance mode, powders scraped from electrodes.) Fig. 2 compares impedance spectra of LiMn_2O_4 and LiNiO_2 in $\text{LiC}(\text{SO}_2\text{CF}_3)_2$ and LiPF_6 solutions in EC–DMC mixtures. After being in contact with LiPF_6 solutions, the XPS spectra of these electrodes, even in their discharged, fully lithiated state, clearly show the presence of LiF on their surface. The spectral studies presented in Fig. 1, XPS analysis of cathodes and the impedance data, part of which are demonstrated in Fig. 2, converge to the following conclusions regarding the cathodes' side in Li-ion batteries.

1. Pristine LiNiO_2 and LiCoO_2 are often covered by surface Li_2CO_3 (see typical peaks around 1500–1400 and 880 cm^{-1} in the relevant spectra of Fig. 1. These electrodes are covered in solutions by surface films whose spectra resemble those of ROCO_2Li species and polycarbonates. We propose that such surface species can be formed on the cathodes by possible nucleophilic attacks of the negatively charged oxygen atoms of the LiNiO_2 or LiCoO_2 surfaces on solvent, alkyl carbonates molecules, that are all strong electrophiles. Such attacks should form surface alkyl carbonate groups. Surface nucleophilic reactions can also lead to anionic polymerization of alkyl carbonates (mostly EC) that may form on the cathodes' surface chains of poly EC.
2. From both the FTIR and XPS data, it is clear that LiMn_2O_4 is less reductive with solution species than LiCoO_2 and LiNiO_2 .
3. LiCoO_2 and LiNiO_2 always have a high concentration of LiF on their surface as compared with LiMn_2O_4 , after being exposed to LiPF_6 solutions.
4. The impedance of LiCoO_2 and LiNiO_2 electrodes is usually higher than that of LiMn_2O_4 in the same solutions. In addition, the impedance of all the electrodes is higher in LiPF_6 solutions than in any other salt solutions.
5. Hence, we concluded that LiNiO_2 and LiCoO_2 are more nucleophilic and basic than LiMn_2O_4 , at least on their particle surfaces, and thus they react more readily with solution species (nucleophilically with the alkyl carbonates and as bases with HF). Hence, their impedance is higher due to the impact of the surface films on the transport of Li-ions. However, this reactivity of LiNiO_2

and LiCoO_2 is not necessarily bad. Organic surface films should protect the cathode materials from reactions with acidic species in solutions, which are detrimental because they lead to the dissolution of the transition metal.

Fig. 3 relates to the study of aging of Li–graphite/EC–EMC + $\text{LiPF}_6/\text{LiCoO}_2$ battery systems. It compares the impedance spectra of pristine and cycled graphite and LiCoO_2 electrodes in one of the conventional, commonly used electrolyte solutions, EC–EMC/ LiPF_6 . The electrodes were cycled and stored at 60 °C before the EIS measurements. Fig. 3 demonstrates that the electrodes' impedance increases considerably due to their cycling and storage at 60 °C. The impedance of the LiCoO_2 cathode was even more affected by the electrochemical operation, and proportionally increased more than that of the graphite electrode.

We conducted EQCM experiments with EC–EMC/ LiPF_6 solutions separated from Li– LiCoO_2 cells after cycling and storage at 60 °C. The working electrode in these experiments was platinum. The voltammograms of these experiments showed sharp cathodic peaks between 2 and 1.5 V (Li/Li⁺) that relate to Co deposition (mass accumulated per electrons transferred was around 30 g/mol, which is equal to the equivalent weight of cobalt in the following process: $\text{Co}^{2+} + 2e^- \rightarrow \text{Co}^0$). XPS studies of the Li counter electrodes in these cells showed clear evidence of cobalt deposition on it (typical cobalt peaks around 780 eV). Fig. 4 compares XRD patterns of pristine and cycled cobalt electrodes. This figure shows no changes in the bulk structure of cycled/stored electrodes at elevated temperature (60 °C). Studies of cycled graphite anodes by XRD also show no pronounced changes in their bulk structure upon cycling/storage at elevated temperatures. Hence, we find that the cobalt dissolution observed does not affect the bulk electrodes, and probably relates to surface phenomena. It also appears that the major detrimental process of both graphite and LiCoO_2 electrodes during prolonged cycling/storage at elevated temperatures relates to changes in their surface films that increase their impedance. Impedance increase upon storage/cycling at elevated temperatures seems to be the major cause for capacity-fading at elevated temperatures, not bulk changes in the electrode materials.

XRD, XPS, and FTIR studies of graphite and LiCoO_2 electrodes cycled in EC–EMC/ LiPF_6 solutions at elevated temperatures clearly showed a massive formation of LiF on the surfaces of both electrodes, as well as other fluorine and phosphorous compounds, reduction products of the salt anion (probably Li_xPF_y and Li_xPOF_y species). It is well known that the LiF surface films are highly resistive to Li-ion migration. Whenever they are formed, either on Li, Li–graphite or Li_xMO_y electrodes, they lead to high electrode impedance [13]. Hence, in order to improve the high temperature performance of commonly studied Li-ion battery systems (that usually contain LiPF_6 solutions), it is important to reduce the impact of the LiPF_6 salt and its

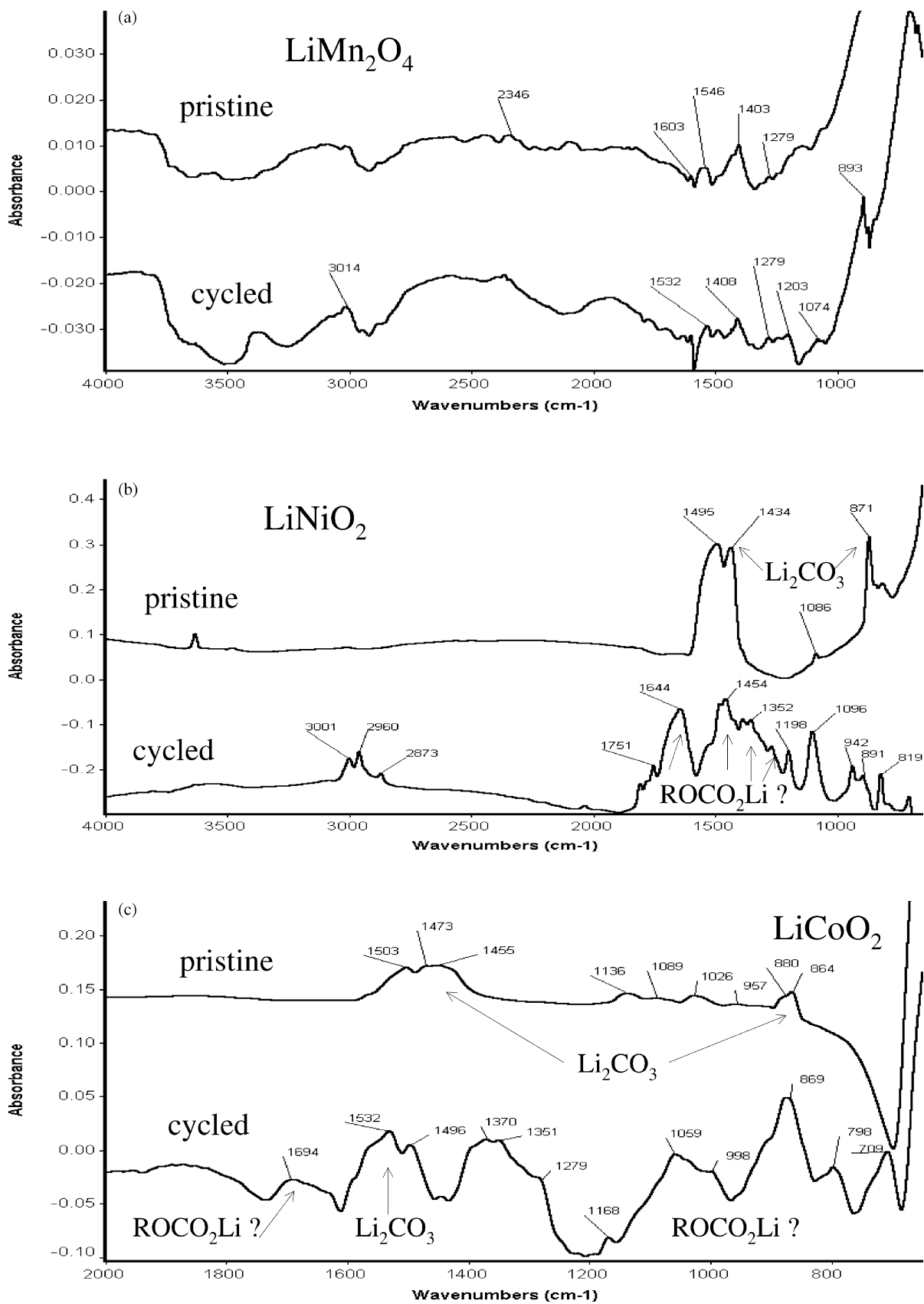


Fig. 1. FTIR spectra measured by diffuse reflectance mode, obtained from pristine and cycled composite LiMn_2O_4 , LiCoO_2 , and LiNiO_2 electrodes, as indicated (EC-DMC/LiAsF₆ solutions).

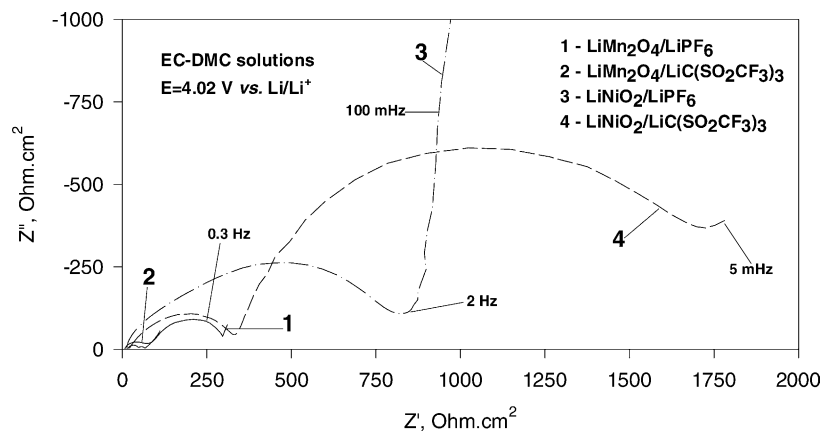


Fig. 2. Comparison of impedance spectra of similar composite LiMn_2O_4 and LiNiO_2 , measured at 4.02 V in LiPF_6 and $\text{LiN}(\text{SO}_2\text{CF}_2)_2$ solutions (EC-DMC), as indicated. The presence of HF in LiPF_6 solutions leads to the formation of highly resistive LiF films. Also note that LiNiO_2 is more reactive with solution species than LiMn_2O_4 .

related contaminants (e.g. HF, PF_5) on the electrodes' surface chemistry.

We studied solutions of four other salts: LiAsF_6 , LiClO_4 , $\text{LiN}(\text{SO}_2\text{CF}_2, \text{CF}_3)_2$ (LiBETI), and $\text{LiPF}_3(\text{CF}_2\text{CF}_3)_3$ (LiFAP), in the commonly used alkyl carbonate solutions (EC with DMC, DEC or EMC, including ternary mixtures) with

graphite anodes, LiCoO_2 and LiMn_2O_4 cathodes. LiAsF_6 and LiClO_4 solutions seem to be very suitable from the performance point of view. They are not acidic, and all the electrodes behave highly reversibly in LiAsF_6 or LiClO_4 solutions. The surface chemistry of graphite electrodes in these solutions is dominated by reduction of EC to species such as $(\text{CH}_2\text{OCO}_2\text{Li})_2$ that precipitate on the electrodes' surfaces as highly passivating and protecting surface films. Nevertheless, neither LiAsF_6 nor LiClO_4 seem to be relevant to practical batteries. The former salt contains arsenic and the latter salt is not stable at elevated temperatures. The performance of graphite electrodes in $\text{LiN}(\text{SO}_2\text{CF}_2, \text{CF}_3)_2$ solutions is rather poor, especially at elevated temperatures. LiFAP solutions seem to be the most promising for Li-ion batteries from all the other solutions that we studied:

1. Their thermal stability is higher than that of LiPF_6 solutions [17].
2. Graphite electrodes exhibit very high cyclic efficiency in LiFAP solutions, especially at high temperatures ($>60^\circ\text{C}$).
3. The performance of LiMn_2O_4 electrodes is better in LiFAP than in LiPF_6 solutions.
4. It was confirmed that LiFAP solutions are not acidic. The surface chemistry of both graphite and LiMn_2O_4 electrodes in LiFAP solutions is dominated by reactions of solvent molecules, which form protective films on them.

The remaining question is whether Merck, the producer of this salt, is able to produce and distribute LiFAP solutions at reasonable prices.

We tested additives that may positively affect the surface chemistry of graphite anodes and Li_xMO_y cathodes.

We report briefly on three examples: vinylene carbonate (VC), Li di salicylate-borate (denoted as LDSB), and dimethyl pyrocarbonate. In our studies, we confirmed that VC is a desirable additive in electrolyte solutions for Li-ion batteries, as was previously reported [18]. VC can polymerize

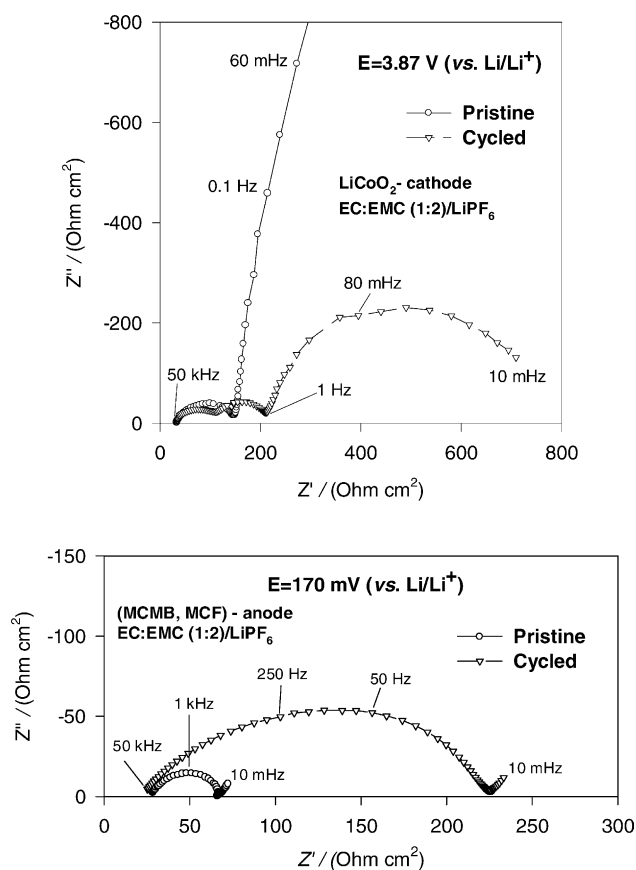


Fig. 3. Comparison between impedance spectra of pristine and aged graphite and LiCo_2 electrodes, EC-EMC/ LiPF_6 1 M solutions. Aging included charge-discharge cycling and storage for a few weeks at 60°C . The impedance spectra were measured at 25°C .

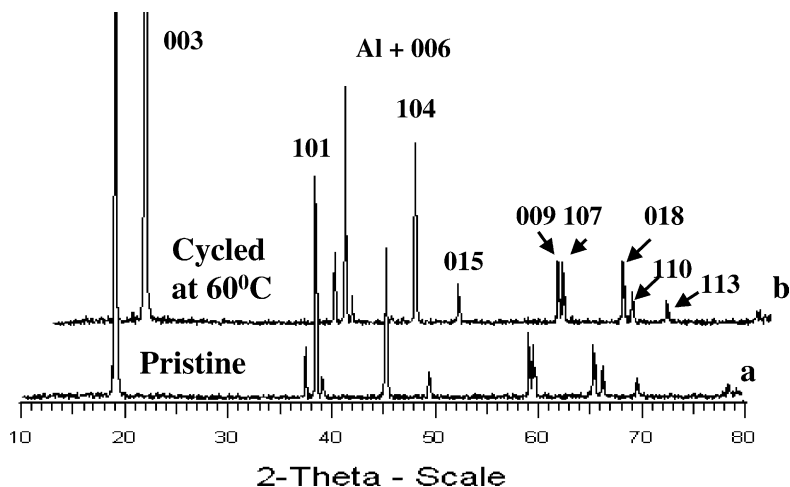


Fig. 4. XRD patterns of a pristine and aged LiCoO_2 electrode. The aging included charge–discharge cycling and storage at 60°C in an EC–EMC/ LiPF_6 solution. (a) A pristine electrode; (b) a cycled and aged electrode.

on graphite or Li_xMO_y electrode surfaces, either via the double bond or via the carbonate group and ring opening [19]. Its onset potential of reduction on graphite is higher than that of solvent/salt anion reduction. We found clear evidence for the suppression of salt anion reduction and LiF formation in VC solutions [19]. The presence of LDSB in solutions has a very strong positive impact on the performance of Li –graphite anodes, and LiCoO_2 and LiMn_2O_4 cathodes. The presence of this additive reduces the impedance of all the above-mentioned electrodes in the temperature range that we measured, i.e. 25 – 60°C . A pronounced suppression of all possible PF_6^- , PF_5 and HF reactions on the electrodes was clearly indicated by spectroscopic studies. The kinetics of both Li –graphite anodes and LiCoO_2 or LiMn_2O_4 cathodes usually become very sluggish during prolonged storage at elevated temperatures ($<45^\circ\text{C}$), because of an increase in their impedance (due to intensive surface reactions related to the LiPF_6 salt). However, when LDSB is present in solutions, even at less than 1% (w/w), the kinetics of LiCoO_2 electrodes after cycling and storage remain fast, and very similar to that of the pristine electrodes.

We also found a very positive effect to the presence of dimethyl pyrocarbonate in LiPF_6 solutions ($<5\%$ v/v) on the performance of graphite electrodes at elevated temperatures (80°C). We assume that a positive impact of the presence of this additive in solutions is its decomposition at high temperatures, which liberates CO_2 . CO_2 reacts on Li and Li-C surfaces to form Li_2CO_3 , which was found to be a very good passivating agent for lithiated graphite electrodes [13].

4. Conclusions

The electrochemical behavior of both lithiated carbon anodes and lithiated transition metal electrodes is controlled

by complicated surface chemistry. On the anode side, the low potential continuously drives the reduction of solution species. On the cathodes, there is no electrochemical driving force for electrode–solution reactions. However, there are spontaneous surface reactions such as acid–base interactions between the basic Li -oxides and HF and other acidic species, or nucleophilic reactions between the negatively charged oxygens of the Li_xMO_y species and the electrophilic alkyl carbonate molecules. Cycling and/or aging of Li graphite and LiCoO_2 electrodes in LiPF_6 solutions at elevated temperatures enhances the above described surface reactions, especially those related to the LiPF_6 salt and its attached contaminants. This leads to an increase in the electrodes' impedance, which is a major cause for capacity-fading at high temperatures. Replacement of LiPF_6 by salts, which do not form acidic contaminants, or the use of additives that predominantly react on the electrodes' surface and block reactions of acidic species, should improve the performance of Li -ion batteries. Polymers forming additives may be considered. However, the polymers have to enable facile Li -ion transport through them. VC and Li di salicylate-borate salt were found to be suitable additives. We assume that these additives are successful because their reactions on the electrodes form surface species which are poly Li salts.

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