

Key factors for the cycling stability of graphite intercalation electrodes for lithium-ion batteries

Felix Joho ^{a,*}, Beat Rykart ^a, Roman Imhof ^{a,1}, Petr Novák ^a, Michael E. Spahr ^b,
Alain Monnier ^b

^a Paul Scherrer Institute, Electrochemistry Section, CH-5232 Villigen PSI, Switzerland
^b TIMCAL, CH-5643 Sins, Switzerland

Abstract

Aspects of the charge loss during the first cycle and the cycling stability of lithium-ion batteries are discussed as functions of water and oxygen impurities in their electrolyte solutions. Differential electrochemical mass spectrometry revealed different decomposition products depending on the water content. Carbon black, copper particles, and nickel particles were added to the graphite electrodes in order to improve their cycling stability. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Commercial lithium-ion batteries with high energy density and good cycleability usually consist of a carbon-based negative electrode, a positive lithium metal oxide electrode, and a separator soaked with an organic electrolyte. Despite the high level of development of the batteries several unsolved problems remain. One of them is the rather high irreversible charge loss occurring during first charging of the carbon electrodes [1]. It is generally accepted that this charge loss is mainly due to reductive decomposition of the electrolyte on the negative electrode [2]. The resulting protective film, called solid electrolyte interphase (SEI), allows lithium-ion transfer but prevents electron transfer [3,4]. The SEI formation mechanism is rather complex and not yet completely understood. In the present work the influence on SEI formation of different amounts of water as well as oxygen in the electrolyte was studied in electrolyte solutions based on ethylene carbonate (EC) and dimethyl carbonate (DMC). Moreover, the composition of the electrode influences the cycling stability. We have studied the influence of several additives to minimize the charge loss during cycling.

2. Experimental

The standard procedure for graphite electrode preparation was as follows: A slurry of the particular graphite, TIMREX SFG 6 or TIMREX SFG 44 (TIMCAL AG), polyvinylidene fluoride (PVDF), and 1-methyl-2-pyrrolidone was sprayed on heated titanium or stainless-steel current collectors. After evaporation of the solvent the electrodes were dried at 120°C under dynamic vacuum for at least 15 h.

The electrochemical studies were performed in hermetically sealed two-electrode cells with an oversized lithium counter-electrode. The cell components were arranged as in button cells, as published elsewhere [5]. A lithium reference electrode was used for few special experiments with high water or high oxygen content in the electrolyte solution. The electrodes were separated by a glass fiber separator soaked with the electrolyte, 1 M LiClO₄ in EC + DMC (1:1 by volume). All chemicals for the electrolyte solution were purchased from Merck and used as received. The graphite electrodes were galvanostatically cycled between 1.5 and 0.005 V vs. Li/Li⁺. The first cycle was performed at a slow rate of ±0.01 mA/mg (related to the graphite mass). The subsequent cycles were performed at a faster rate of ±0.05 mA/mg. At 5 mV vs. Li/Li⁺ the current was always lowered potentiostatically to 0.005 mA/mg.

* Corresponding author.

¹ Present address: Renata AG, CH-4452 Itingen, Switzerland.

The electrolytes were contaminated as follows: (a) Water was added in the glove box by a syringe. The water content was determined by the Karl-Fischer method with a KF Coulometer 684 (Metrohm). (b) The electrolyte solution was saturated with oxygen, which was dried over activated molecular sieve. The differential electrochemical mass spectrometry (DEMS) measurements were performed as described in Ref. [6]. When investigating the different additives the electrodes were prepared as follows: The carbon black (Cabot XC 72) was added to the slurry of graphite and binder, then the slurry was thoroughly mixed and sprayed on the heated current collector. Raney copper and Raney nickel (Fluka) stored under water were mixed with TIMREX SFG 44 and PVDF dissolved in 1-methyl-2-pyrrolidone. The sprayed electrodes with metal additive were dried under dynamic vacuum as soon as possible to minimize oxidation of the metal.

3. Results and discussion

In our attempt to identify the key factors of SEI formation on the graphite electrode, we report here on our investigations concerning the influence of water and oxygen in electrolyte solutions and the effect of additives on the cycleability of graphite electrodes. The studies related to electrolyte contamination were performed with the graphite TIMREX SFG 6 (BET specific surface area: 15 m²/g), because we expected that SEI-related effects are more pronounced with graphites having a high specific surface area and exhibiting therefore a high charge loss [2]. For lithium-ion battery applications, of course, graphites with a smaller charge loss during the first cycle will be preferred. Therefore, in the second part of this work, we studied the influence of the additives also on TIMREX SFG 44 (BET specific surface area: 4.3 m²/g), since it exhibits a lower charge loss in the first cycle (~10%). The reversible specific charge for all SFG graphites is close to the theoretical value of 372 A h/kg (based on the

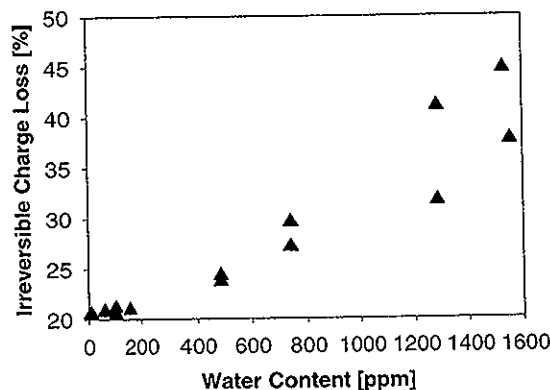


Fig. 2. Dependence of the irreversible charge loss of the graphite SFG 6 during the first cycle on the water content in the electrolyte (cell Li/1 M LiClO₄ in DMC+EC/SFG 6).

graphite weight), and the cycleability with lithium as counter-electrode is reasonable, as shown in Fig. 1.

3.1. Influence of trace water and oxygen in the electrolyte

One aim of this work was to investigate the influence of water and oxygen as common impurities in electrolyte solutions on the cycling performance of graphite electrodes. In an effort to obtain comparable values, we tried to assemble cells with a constant graphite-to-electrolyte ratio. It was important that the irreversible charge loss was measured always exactly under the conditions described in Section 2, because different cycling conditions give different irreversible charge losses. We chose slow cycling conditions for the first cycle. Therefore, most of the irreversible charge loss occurred during the first cycle. In a dry electrolyte (≈ 8 ppm H₂O) the irreversible charge loss caused by SFG 6 as active electrode material was about 20% during the first cycle. This quantity is defined by formula (1) below. It increased gradually with increasing water content (Fig. 2). The large scatter of the values for higher water contents is probably due to the influence of

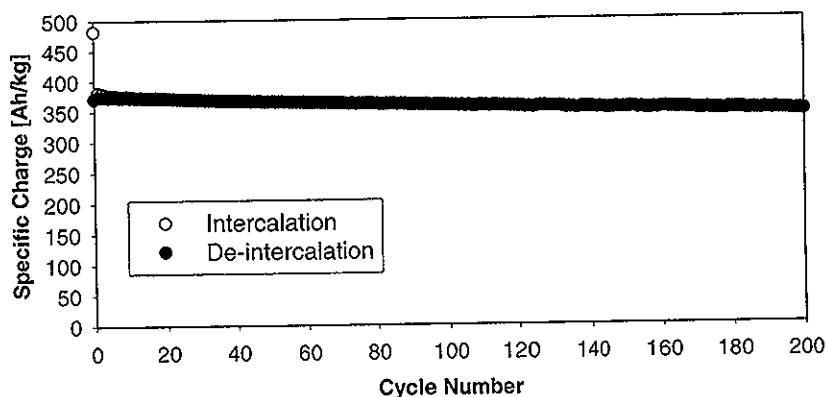


Fig. 1. Cycling performance of a negative electrode containing the graphite TIMREX SFG 6 with 5% carbon black, measured vs. lithium metal in the electrolyte 1 M LiClO₄ in DMC + EC. The cycling rate was $\sim C/7$, and the specific charge is based on the weight of the graphite only.

the lithium counter-electrode, which also reacts with trace water. Therefore, we presume that for high water contents the charge loss in the first cycle will be even higher in complete lithium-ion cells, where metallic lithium is absent and the trace water will be reduced only at the negative carbon electrode.

$$CL = \frac{C_{\text{int}} - C_{\text{de-int}}}{C_{\text{int}}} \times 100\% \quad (1)$$

CL: charge loss; C_{int} : charge of the intercalation reaction including SEI formation; $C_{\text{de-int}}$: charge of the de-intercalation reaction

Cycling tests with up to thirty cycles were made, but we could not see any clear dependence of cycling stability on the amount of trace water. So we cannot confirm that electrolytes containing several hundred ppm of water have an improved cycling stability over dry electrolytes, as was suggested in the literature [7] for the electrolyte 1 M LiAsF₆ in DMC + EC.

Differential electrochemical mass spectrometry (DEMS) measurements clearly showed that in a dry electrolyte considerably less hydrogen gas is produced (Fig. 3). The higher the trace water content of the electrolyte solution, the more hydrogen gas ($m/z = 2$) is detected during the first cycle. Hydrogen evolution starts at about 1.3 V vs. Li/Li⁺ during the first intercalation and is explained by water reduction. This observation agrees with the results of cycling experiments in which additional charge was consumed during the first cycle, probably due to additional water decomposition. The observation that the amount of evolved ethylene ($m/z = 27$) decreases with increasing water content implies that the SEI is built up differently depending on the amount of water present. The SEI probably contains more lithium salts, when the water content is

high. Whereas, if the water content is low, the SEI contains more decomposition products of the organic carbonates. However, as discussed above, the cycling experiments revealed no clear correlation between the fading of the capacity and the water content.

In preliminary experiments we had exposed the electrolyte solution to the atmosphere in order to pollute the electrolyte solution with water. But the correlation of Fig. 2 could not be found in this way, because oxygen also influences the performance of Li/graphite cells. Therefore, we investigated the influence of oxygen as another common pollutant in the electrolyte solutions. Our experiments showed that cells with an electrolyte solution which had been exposed to the oxygen atmosphere exhibited significantly inferior cycleability and a higher irreversible charge loss during the first cycle than cells with an electrolyte solution to which only water was added. This deterioration of the cycling behavior is mainly due to the higher resistance of the lithium counter-electrode. If the cycling of the cell is controlled by the potential between working and reference electrode, the cycling behavior is comparable to one of our usual cycling experiments (Fig. 4). Therefore, we think that oxygen predominantly interferes with the lithium metal counter-electrode. Thus, in a two-electrode arrangement the cycling stability of the cell is deteriorated.

3.2. Influence of carbon black and metal particle additives on the performance of graphite electrodes

It is an experimental fact that the resistance of the negative carbon electrode increases during cycling [8]. This problem should be diminished by adding an electronically well conductive additive. We compared the perfor-

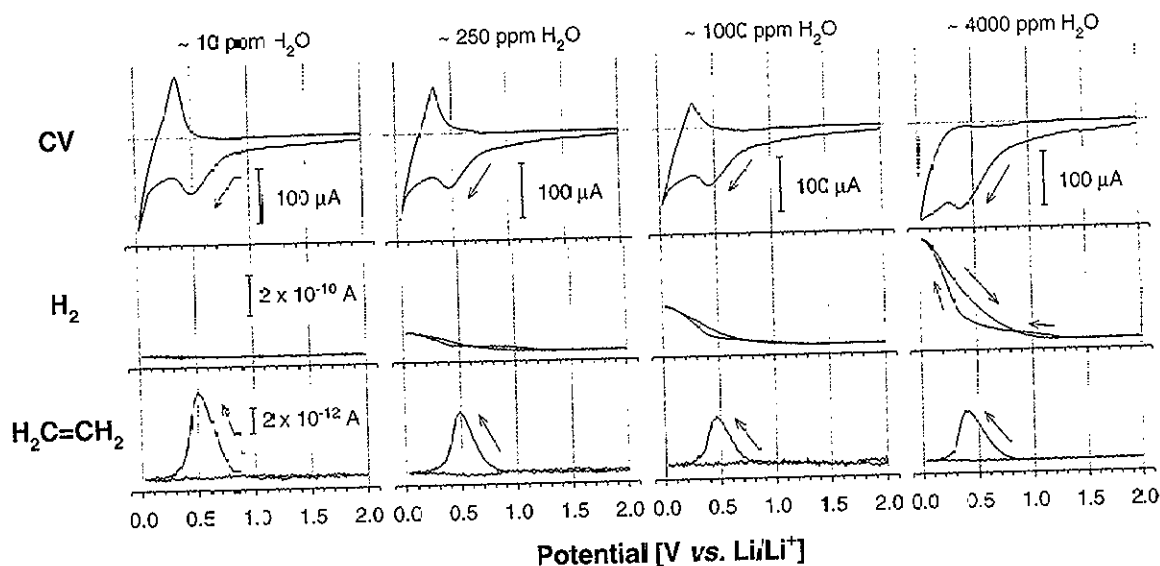


Fig. 3. Influence of water concentration in the electrolyte solution on the decomposition of 1 M LiClO₄ in DMC + EC: Cyclic voltammogram (CV) at 0.4 mV/s (first cycle) of the graphite SFG 6 and simultaneously recorded mass spectrometry cyclic voltammograms for the evolution of hydrogen (H₂) represented by $m/z = 2$ and ethylene (H₂C=CH₂) represented by $m/z = 27$.

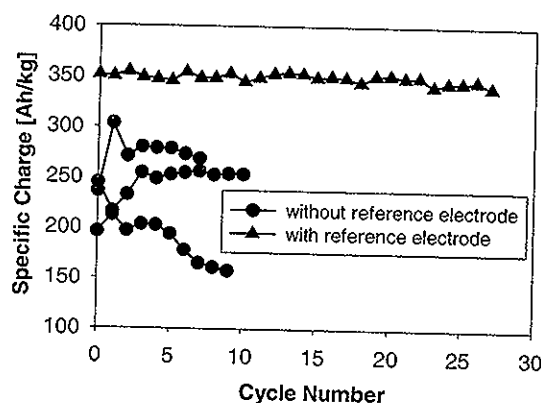


Fig. 4. Cycling performance of Li/1 M LiClO₄ in DMC+EC/SFG 6 cells with oxygen-saturated electrolyte solution, as measured with and without a lithium reference electrode.

mance of the additives by cycling the electrodes about 100 times in order to establish distinct trends. We defined a normalized capacity loss as in formula (2) below to compare the capacity losses of different cells. The highest de-intercalation charge, C_h , was usually recorded in the second cycle, but sometimes the de-intercalation charge of the first or third cycle was slightly higher. By adding carbon black as an additive, the cycle life of the negative electrode is improved and the capacity fading is smaller. However, be aware that the experimental curves still overlap (Fig. 5). The effect of carbon black is especially pronounced under conditions where the theoretical capacity of the graphite is not reached [9,10].

$$L_{\text{cap}} = \left[1 - \frac{C_n}{C_h} \right] \times 100\% \quad (2)$$

L_{cap} : capacity loss; C_n : de-intercalation charge of a particular cycle; C_h : highest de-intercalation charge

We also investigated fine metal particles as additives for graphite electrodes. We chose fine copper and nickel particles as the additives. For this investigation we used

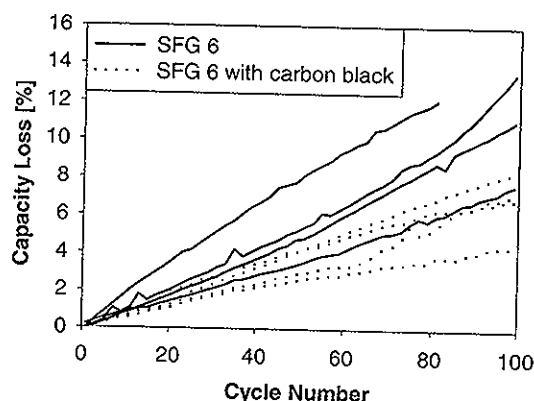


Fig. 5. Comparison of the capacity losses during galvanostatic cycling at a $\sim C/7$ rate of several SFG 6 electrodes with and without the carbon black additive (electrolyte 1 M LiClO₄ in DMC+EC; lithium counter-electrode).

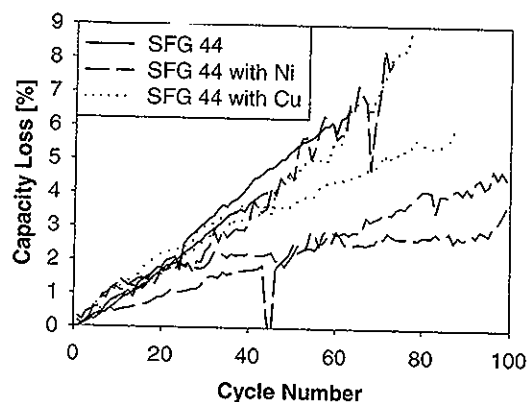


Fig. 6. Comparison of the capacity losses during galvanostatic cycling at a $\sim C/7$ rate of several SFG 44 electrodes without and with the metal additives copper and nickel (electrolyte 1 M LiClO₄ in DMC+EC; lithium counter-electrode).

the graphite TIMREX SFG 44, which differs from TIMREX SFG 6 by its particle size distribution. The BET specific surface area and the irreversible charge loss during the first cycle are much smaller for SFG 44. The conductivity of SFG 44 is slightly lower, and therefore the effect of a metal additive may be more pronounced.

The influence of the metal additives, copper and nickel, is shown in Fig. 6. Generally, the cycling stability is improved. This agrees well with the results of other authors, who used silver, gold, or other metals as additives and/or coatings [11–13]. (Be aware that metal additives like Ag and Au improve the cycling stability and, in addition, the energy density, since these metals alloy with lithium [1].) In our experiments the electrodes with nickel metal particles as the additive usually have a better cycling stability than the electrodes with copper particles. A possible explanation may be found in the different surface oxides present on these metals. Copper oxide impurities on copper metal were detected during the first galvanostatic discharge by the appearance of two additional plateaus (Fig. 7) at about 1.6 V and 1.2 V vs. Li/Li⁺ (attributed to CuO/Cu₂O reduction [14]), whereas the reduction of nickel oxide was not revealed by additional plateaus. The

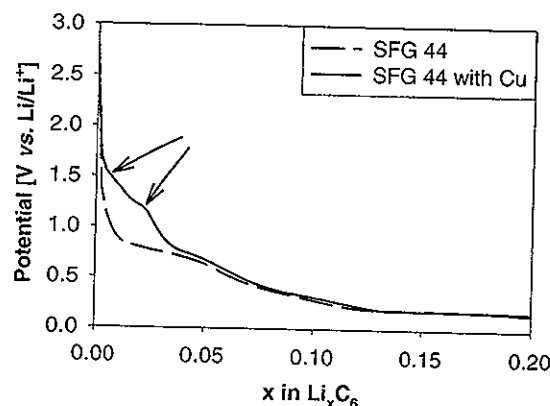


Fig. 7. Comparison of the first charge curves of graphite SFG 44 with and without the copper additive.

additional irreversible charge loss was 4% for the nickel and 6% for the copper additive, which was therefore assigned to the reduction of copper oxides or nickel oxides, respectively. However, in spite of their oxide impurities, the metal additives improve the cycleability of graphite electrodes to some extent.

4. Conclusions

The presence of trace water in the electrolyte solution of lithium-ion batteries increases the irreversible charge loss in the first cycle due to water reduction. No correlation between water content and cycling stability could be found. Conductivity-enhancing additives such as carbon black or metal particles may prolong the cycle life of a negative graphite electrode by reducing the increase of resistance of the electrode occurring during prolonged cycling.

Acknowledgements

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