

Short communication

Study of styrene butadiene rubber and sodium methyl cellulose as binder for negative electrodes in lithium-ion batteries

H. Buqa^{a,*}, M. Holzapfel^a, F. Krumeich^b, C. Veit^c, P. Novák^a

^a Paul Scherrer Institut, General Energy, 5232 Villigen PSI, Switzerland

^b ETH Zürich, Laboratory of Inorganic Chemistry, Hönggerberg HCI-G105, 8093 Zürich, Switzerland

^c Degussa AG, Paul-Baumann-Str. 1, Building 1420/18, DE-45764 Marl, Germany

Received 17 January 2006; received in revised form 27 March 2006; accepted 28 March 2006

Available online 26 May 2006

Abstract

Graphite and nano-silicon-based negative electrodes in lithium-ion batteries with low binder content were evaluated. The effectiveness of styrene butadiene rubber (SBR) and various types of cellulose containing electrodes were compared to standard electrodes containing PVdF as binder. The cycling performance of lithium-based half cells in EC:DMC (1:1), 1 M LiPF₆ shows that styrene butadiene rubber (SBR), sodium carboxymethyl cellulose (Na-CMC), or both combined have a similar bonding ability as conventional poly(vinylidene fluoride) (PVdF). However, using Na-CMC the irreversible charge capacity in the first cycle decreased in comparison with electrodes containing PVdF binder. Nano-Si electrode containing 1% SBR/1% Na-CMC as binder show the same cycle stability as an identical electrode containing 10% PVdF binder.
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Keywords: Lithium-ion battery; Graphite; Nano-silicon; Styrene butadiene rubber; Cellulose; *Post mortem* SEM

1. Introduction

Lithium-ion batteries are becoming more and more important in the world market of energy devices, with respect to their energy density, which is amongst the highest for any known secondary battery system (up to more than 150 Wh kg⁻¹). For large size applications such as in EV or HEV, both higher energy density and low-cost materials are required. In order to enhance the performances of lithium-ion batteries, researchers and battery-manufacturers are trying to create new electrode materials, new electrolytes, and new additives. However, battery efficiency is strongly dependent on the electrode engineering [1–3]. An important approach to improve the behaviour of lithium-ion batteries is the optimisation of the binder used for the electrode preparation, which should meet various requirements. The role of binders becomes increasingly important in terms of energy density of the whole battery. It is desirable to reduce the binder content, whilst at the same time maintaining the required properties and functionality of the electrode. Beyond its chemical

and electrochemical stability in electrode/electrolyte interactions, the binder has to survive the large repeated dimensional changes of the electrode during the cycling of the cell. In commercial lithium-ion batteries, poly(vinylidene fluoride) (PVdF) has been used as binder for both the negative and positive electrodes because of its good electrochemical stability and high adhesion to the electrode materials and current collectors [3].

An interesting approach to improve the energy density of the negative electrodes for their use in lithium-ion batteries is the mixing of active materials with only small amounts of binder materials [4–6]. Especially appealing would be to lower the content of a binder for a nano-silicon-based electrode [7]. The main disadvantage of all alloy-based electrodes is the huge volume change which occurs upon the insertion/deinsertion of the lithium into and from alloying the host material. The volume change of both silicon and tin-based alloy electrodes is around 200–300% [8]. This leads to pronounced mechanical fatigue upon prolonged cycling, as the particles break-up and become non-contacted. Capacity loss and cycle life of, e.g. composite silicon-based electrodes is known to depend on many variables, including the amount of Si in the electrode formulation, binder properties, and electrode engineering [9,10]. Most of the published work on binders deals with the testing of new binder

* Corresponding author. Tel.: +41 56 310 4406; fax: +41 56 310 4415.
E-mail address: hilmi.buqa@psi.ch (H. Buqa).

materials and their interactions with the active materials and the electrolyte [11]. It was also shown that the binder amount and electrode engineering had influence on the electrochemical performance of tested electrodes [12]. In this paper, the role of styrene butadiene block co-polymer (SBR) and sodium carboxy methylcellulose (Na-CMC) as binders for TIMREX[®] SFG synthetic graphite and nano-silicon-based negative electrodes has been investigated and analysed in order to improve the electrodes, their capacity and cycle life. Note that SBR possesses higher flexibility, stronger binding force, and higher heat resistance than the widely used PVdF [10]. Moreover, Na-CMC and SBR are soluble in environmental friendly solvents such as water [13] and ethylacetate, respectively, which is of importance for the future electrode production.

In this work, test electrodes were prepared combining various kinds of binders: PVdF, SBR, Na-CMC, mixtures of SBR and Na-CMC, ethyl cellulose, and methyl cellulose. The electrochemical performances of the obtained electrode composites, with different binder contents were tested and compared. In order to get a direct view on the effect of the binders on the SEI-film formation and cycling process, scanning electron microscopy (SEM) analyses of cycled and uncycled electrodes were performed.

2. Experimental

TIMREX[®] SFG (TIMCAL SA, Bodio, Switzerland) graphite powders and Si-based electrode materials were used as negative electrode. Two TIMREX[®] SFG graphites with different particle size (SFG6 and SFG44 having d_{90} values of 6 and 44 μm , respectively) were used as received [14]. The silicon composite material was prepared by direct mixing of nano-scale silicon (Degussa, Marl, Germany) with graphite TIMREX[®] KS6 and carbon black SP (TIMCAL SA, Bodio, Switzerland). The idea of such electrode preparation method was pursued by us (see Deiss et al. [15]), but we improved the procedure using different graphite and carbon black materials. The best results were achieved using KS6 graphite and SP carbon as conductive materials for the silicon composite electrodes. The test electrodes were prepared by blade-coating the graphite on a copper foil with different binders. The SBR (Dow Chemicals, Horgen, Switzerland) was dissolved in ethyl acetate, Na-CMC (Fluka AG, Buchs, Switzerland) and methylcellulose (Selectchemie AG, Zürich, Switzerland) were applied as aqueous solutions and ethyl cellulose (Selectchemie AG, Zürich, Switzerland) was dissolved in ethanol. Various amounts of binder were added to the composite materials. During the slurry preparation with Na-CMC, methyl cellulose, and ethyl cellulose as binders, the viscosity of the slurry was carefully controlled in order to get a uniform dispersion (no agglomeration) between the binder and the electrode materials because cellulose is not completely soluble in water. For comparison, PVdF-bound graphite and Si-based electrodes were prepared as follows: a mixture of 10% nano-Si powder, 5% super P carbon black additive, 75% KS6 graphite for conductivity enhancement, and 10% SOLEF[®] poly(vinylidene fluoride) (PVdF) binder (Solvay SA, Belgium) was dispersed in *N*-methyl pyrrolidone (NMP, Fluka AG, Buchs, Switzerland)

and homogenised for 4 h. The resulting slurry was mixed thoroughly, and cast on a copper foil which serves as a current collector and dried in vacuum at 120 °C for 12 h. The final thickness of the active material on the Cu-substrate was in the range of 80–120 μm , whilst the geometric surface area was always 1.3 cm^2 . The typical loading of a nano-silicon electrode was 4–5 mg cm^{-2} , based on the weight of both carbon and silicon.

The electrochemical measurements were performed in titanium two-electrode cells that were vacuum dried before assembly at 120 °C over night. The galvanostatic measurements of graphite electrodes were performed against a lithium counter electrode at a low current density of 10 m Ag^{-1} of carbon to allow for the complete formation of the solid electrolyte interphase (SEI), which protects the electrolyte from continuous reduction at low potentials. After a potential of 5 mV versus Li/Li⁺ was reached, the charging was continued potentiostatically until the specific current dropped below 5 m Ag^{-1} . A moderate C/5 rate (74.4 m Ag^{-1}) was chosen for the following three cycles to ensure that the SEI-film formation was completed. The nano-silicon electrodes were cycled in the same way, using currents based on the total weight of both carbon and silicon. Constant current constant voltage cycling was performed with a current density of 50 m Ag^{-1} , an upper voltage limit of 1.0 V versus Li/Li⁺, and a lower voltage limit of 5 mV versus Li/Li⁺. At the end of each galvanostatic charge/discharge step, a potentiostatic step followed with a reduction of the current, at the fixed upper or lower potential limit, down to a value of 5 m Ag^{-1} . The electrolyte was ethylene carbonate (EC):dimethyl carbonate (DMC) 1:1, in 1 M LiPF₆ with or without 2 or 5% vinylene carbonate (VC) as an electrolyte additive. The solvents used were obtained battery grade from Merck (Darmstadt, Germany); the LiPF₆ was obtained from Stella Chemicals (Japan). The vinylene carbonate (VC) was obtained from Fluka (Buchs, Switzerland). All chemicals were used as received. The electrolytes contained less than 20 ppm of water, as determined by Karl–Fischer-titration. The cells were assembled in an argon-filled glove box, with less than 1 ppm of oxygen and water.

The electrodes for the *post mortem* scanning electron microscopy (SEM) studies were either galvanostatically charged at 10 m Ag^{-1} to 0.3 V versus Li/Li⁺ or cycled as described above and then stabilised at 0.3 V versus Li/Li⁺ for 2 days. Afterwards, the cells were dismantled; the graphite electrodes were washed with dry DMC, and dried in an argon atmosphere. SEM studies were performed on a LEO 1530 Gemini microscope, which was operated at low voltage (usually 1 kV) to achieve a suitable contrast of the surface details in the secondary electron images and to minimise charging of the uncoated samples.

3. Results and discussion

In our previous work, we reported the very stable cycling of SFG44 graphite electrodes using PVdF as a binder [16]. Typically, a reversible charge capacity of about 360 m Ag^{-1} and a coulombic efficiency of 93% is obtained in the first galvanostatic charge/discharge cycle for the SFG44 negative electrode material at a specific current of 10 m Ag^{-1} in the EC:DMC (1:1), 1 M LiPF₆ electrolyte. During the second and subsequent cycles,

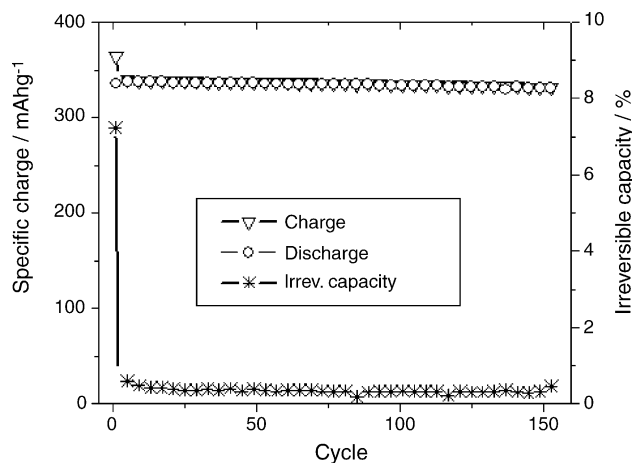


Fig. 1. Cycling performance of a typical graphite electrode (TIMREX® SFG44 with 10% PVdF, measured vs. lithium metal. Electrolyte: EC:DMC (1:1), 1 M LiPF₆, cycling rate $\sim C/7$).

the cycling efficiency increases rapidly from 99 to 99.9%. In Fig. 1, we present a result which is used as a benchmark in this work demonstrating the stable cycling over 150 cycles, with only very small capacity fading. Similar results were achieved using EC:DMC (1:1), 1 M LiPF₆ with 5% VC as electrolyte (not shown).

In this study, three different types of cellulose (Na-CMC, ethyl cellulose, and methyl cellulose) in various proportions were tested as a binder. First, we present the results of Na-CMC. The amount of Na-CMC was varied from 1 to 10%. Fig. 2 shows the long-term cycling behaviour of the SFG44 electrode with 5% Na-CMC binder. The irreversible capacity losses in the first cycle are very low (for the shown cell lower than 3%) and a small fading per cycle was observed. These results confirm the work of Drogenik et al. [5]. Our explanation for the lower irreversible capacity compared to electrodes containing PVdF is based on an interaction (reaction) of surface groups of the carbon with Na-CMC and, therefore, a fast SEI-film formation. The reversible specific charge capacity is ca. 342 mAhg⁻¹ after

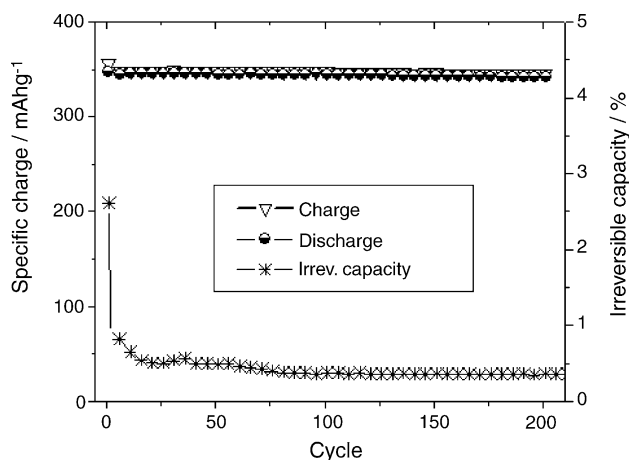


Fig. 2. Cycling performance of a SFG44 graphite electrode in EC:DMC (1:1), 1 M LiPF₆ with 5% vinylene carbonate, using 5% Na-CMC binder.

100 cycles. This is obviously due to the good physical adherence of the graphite particles with Na-CMC binder. In contrast, electrodes prepared using ethylcellulose and methylcellulose as binders, showed poor mechanical stability when the slurry was coated onto the copper foil (results not shown here).

As an alternative binder, we investigated different proportions of SBR in SFG44 graphite electrodes. Using SBR alone, we achieved useful electrochemical results, but the mechanical stability of the electrode after several hundreds of cycles was not satisfactorily (curves not shown in this paper). The reason may be the large particle size of the SFG44 graphite, which may lead to a lower number of anchor points for the SBR. We tried to overcome this challenge via two strategies: (a) Using mixtures of SBR and Na-CMC as a binder, to enhance the mechanical stability of the graphite electrode and (b) using graphite with smaller particle size (here the SFG6 graphite) to enhance the interparticle contact in the electrode.

With the mixtures of SBR and Na-CMC as a binder, satisfactory results were achieved using 1% of SBR and 1% of Na-CMC. The best results with SBR/Na-CMC binder were reached with a mixture of 5% of SBR and 1% of Na-CMC. Results of the long-term cycling are shown in Fig. 3, confirming the very good cycleability of the SFG44 graphite electrode. Low irreversible capacity losses (about 7%) in the first cycle and low fading show that this mixture as a binder combination is very suitable for the graphite electrode. A slightly lower electrochemical charge capacity in comparison to the SFG44 electrode containing PVdF as a binder, however, was observed. The lower value of the electrochemical charge capacity suggests that there is a complex interaction between the two binders (SBR and Na-CMC) and the graphite particles. Possibly, some particles are electrically isolated by the binder mixture and do not take part in the electrochemical reaction. Nevertheless, due to the better adherence forces of the SBR-Na-CMC mixture as binder, the overall cycle life of the SFG44 graphite electrode is improved. Using higher proportions of SBR/Na-CMC (e.g., 8 and 2%), the electrochemical performance of the electrodes deteriorates. Their poor cycleability and electrochemical charge capacity could be due to

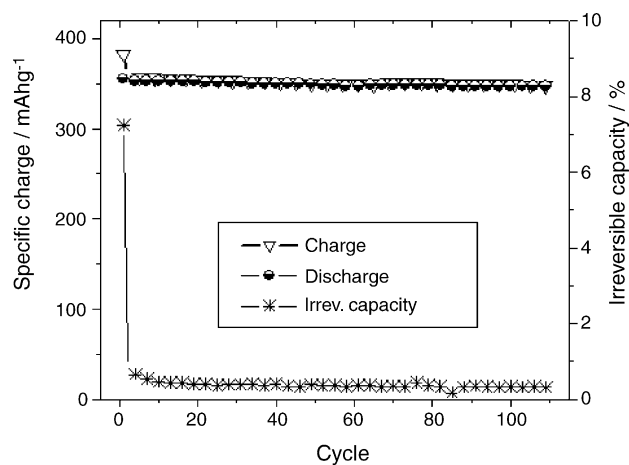


Fig. 3. Cycling performance of a SFG44 graphite electrode in EC:DMC (1:1), 1 M LiPF₆ with 5% vinylene carbonate, using a mixture 5% SBR/1% Na-CMC as a binder.

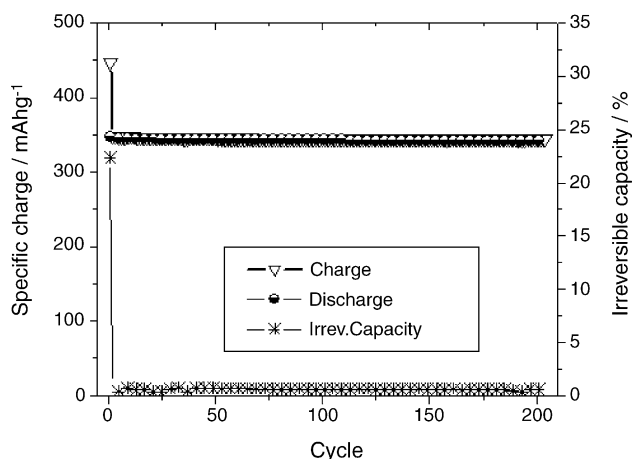


Fig. 4. Cycling performance of a SFG6 graphite electrode in EC:DMC (1:1), 1 M LiPF₆ with 5% vinylene carbonate, using 5% SBR binder.

the electrical insulation of the graphite particles, which hinders the Li⁺-ion diffusion into/from the graphite upon cycling.

Cycling performance of a SFG6 graphite electrode in EC:DMC (1:1), 1 M LiPF₆ with 5% vinylene carbonate, using 5% SBR binder is shown in Fig. 4. The positive effect of the small graphite particle size (SFG6, $d_{90} = 6 \mu\text{m}$) may indicate an improved adherence between the particles, when compared to the case of larger particles (SFG44, $d_{90} = 44 \mu\text{m}$). Improved adherence enhances the electrical contact upon the lithiation/delithiation process, respectively.

Fig. 5 documents the comparable cycling performance (for 100 cycles) for three cells with the SFG6 graphite containing 10% PVdF, 5% SBR, and mixture SBR/Na-CMC (5%/1%), respectively as a binder. Very good cycling behaviour was observed for all three electrodes. Higher capacity upon first cycle and stronger fading was observed for the electrodes containing PVdF binder. No significant differences were observed in the long-term cycleability of all three cells. However, the sta-

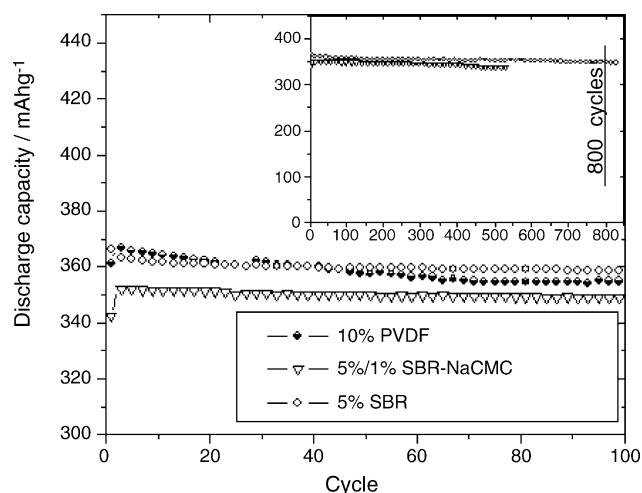


Fig. 5. Enlarged part of the diagram for the first 100 charge/discharge cycles comparing the cycling performance of SFG6 electrodes containing various binders in EC:DMC (1:1), 1 M LiPF₆, with 5% vinylene carbonate. *Inset*: Diagram which documents the long-term stability of SFG6 electrode for over 800 complete charge/discharge cycles (using 5% SBR binder).

bility (lower fading) is slightly better for the cells containing SBR and the SBR/Na-CMC mixture than for the cell containing PVdF. The general features remain also the same, i.e., a relatively low irreversible capacity and low fading of ca. 0.15% per cycle. The inset in Fig. 5 shows that the long-term stability for the electrode containing 5% SBR can be maintained for more than 800 cycles. Stable cycling was also observed for the electrodes containing SBR/Na-CMC (5%/1%) binder for over 500 cycles, with somewhat higher fading. This means that the adherence between graphite particles is enhanced with the SBR and Na-CMC binders, and that the SEI is of higher stability allowing longer cycle life. The lower charge capacity for the mixture SBR/Na-CMC could arise from the higher isolating character of the binder.

To better understand the film formation behaviour and the influence of the binder on the cycleability of graphite electrodes, we performed *post mortem* SEM studies on the electrodes containing the different binders. The electrodes were galvanostatically charged to 0.3 V versus Li/Li⁺ (to assure for a complete SEI-film formation) and subsequently stabilised potentiostatically at this potential for 48 h. A very uniform thin SEI-film is

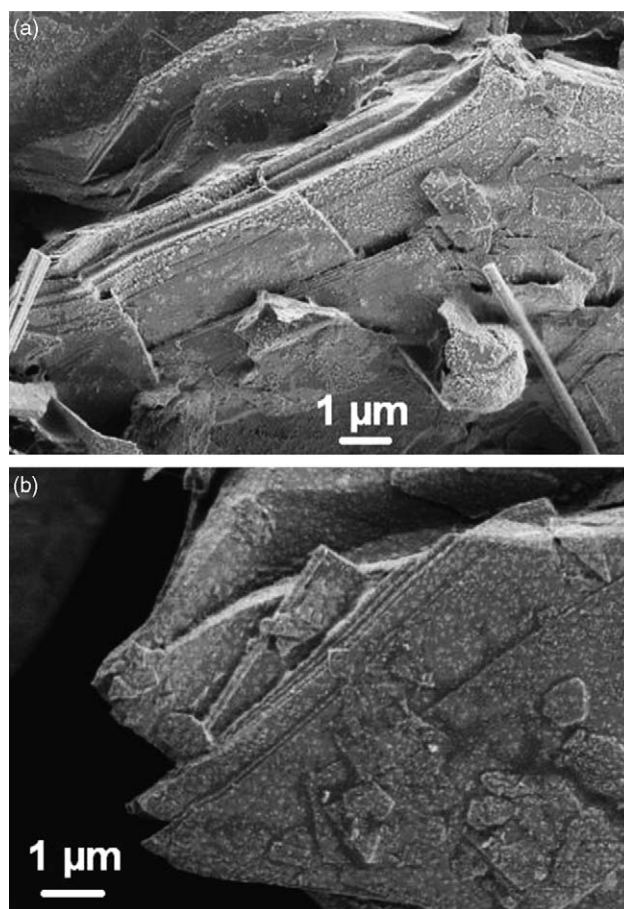


Fig. 6. Post mortem SEM images of a TIMREX[®] SFG44 graphite negative electrode containing 10% PVdF (a) and 5%/1% SBR/Na-CMC (b) as a binder taken from a half-cell after formation of the passivation SEI-film. The electrodes were charged galvanostatically at 10 mAg^{-1} to 0.3 V vs. Li/Li⁺ and stabilised potentiostatically at this potential for 2 days, using 1 M LiPF₆ in EC:DMC (1:1) as electrolyte.

covering the entire graphite surface for both electrodes, shown in Fig. 6a for a PVdF containing electrode and in Fig. 6b for a SBR containing electrode. No significant changes can be observed on the SEI. Note that the binder itself is not visible in the images, which is probably due to its too low scattering power and its small aggregate size. Fig. 7 shows representative *post mortem* scanning electron micrographs of the SFG44 electrodes with PVdF (a) and SBR/Na-CMC (b) binder, which had cycled for 320 cycles. In general, morphological changes of the SEI-film are detectable, but we do not see really important changes, which could directly clarify the influence of the binder on the cycle stability. On both electrodes, a very tight uniform film is observed; all particles are covered with the SEI-film. The *post mortem* images confirm, thus, the good functionality of the electrodes with both types of binders, which makes possible to cycle the graphite electrode in a half-cell configuration, i.e., versus metallic lithium, for over 300 cycles.

The results from the graphite electrodes can be applied to the nano-silicon-based electrodes [17], where we replaced PVdF with SBR and cellulose in the same way as we discussed for the SFG graphite electrodes. Electrodes with various amounts of SBR, Na-CMC, or both mixtures were prepared and galvanostatically cycled. Smaller amounts of such binders are sufficient to

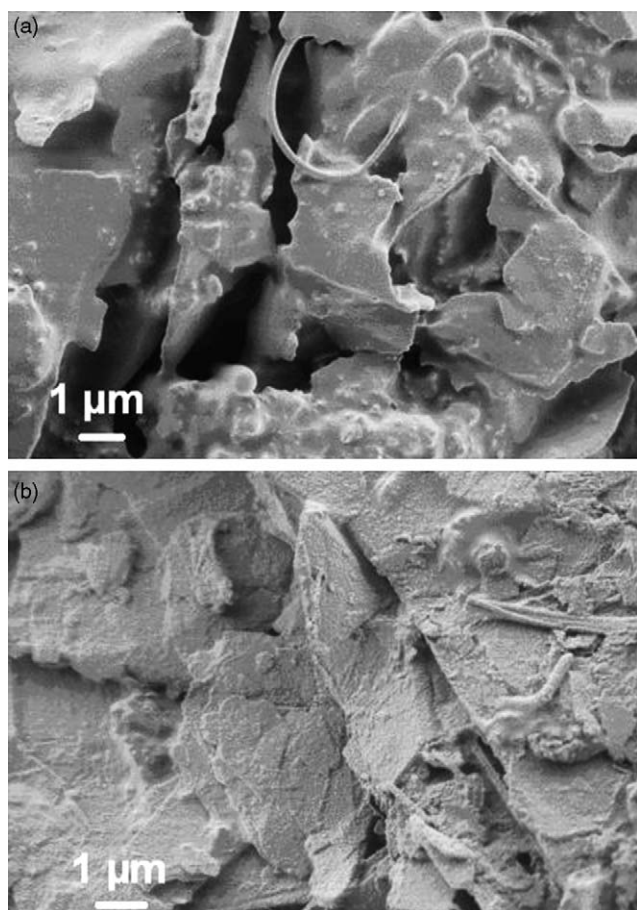


Fig. 7. Post mortem SEM images of a TIMREX® SFG44 graphite negative electrodes containing (a) 10% PVdF and (b) 5% SBR/1% Na-CMC after 320 complete charge/discharge cycles.

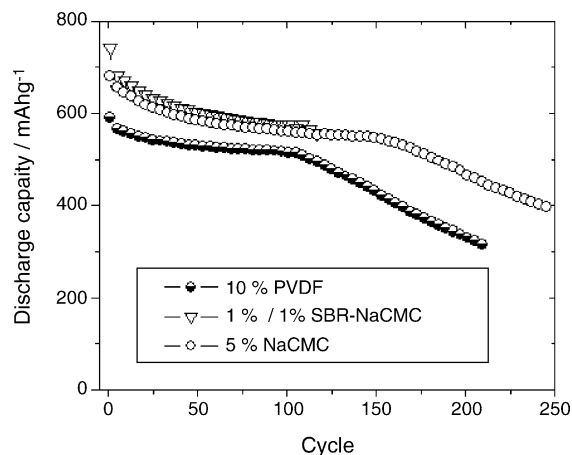


Fig. 8. Comparison of the cycling performance of a 10% nano-silicon containing electrode containing various binders in EC:DMC (1:1), 1 M LiPF₆, with 2% vinylene carbonate.

achieve good electrochemical performances of the nano-silicon electrodes. Fig. 8 documents a comparative long-term cycle life of the Si-based (10% of nano-silicon) electrodes containing PVdF, SBR/Na-CMC (1%/1%), and 5% Na-CMC binder, respectively in EC:DMC (1:1), 1 M LiPF₆ with 2% vinylene carbonate (VC) as electrolyte. The improved cycling performances of the electrodes containing Na-CMC and SBR/Na-CMC binders are apparent, compared to the of PVdF case. The general features remain the same, i.e., a relatively low fading for over 100 cycles. Above 150 cycles the fading is lower for Na-CMC and SBR/Na-CMC containing electrodes with respect to the PVdF binder. This improved cycling stability for nano-silicon composite electrodes with SBR and Na-CMC binder can be explained with the enhanced adhesion strength [7,10] of the binder, which influences the mechanical stability of the Si-based electrode.

4. Conclusion

We have shown that SBR and Na-CMC either alone, or in combination, show a similar bonding ability as the conventional PVdF binder, and that negative electrodes bonded by these binders have nearly the same cycleability. However, using Na-CMC as binder the irreversible charge losses in the first cycle of SFG graphites are lower than for PVdF as binder. Low fading and low irreversible capacity losses upon the cycling for the SFG6 graphite electrode were attributed to the very low particle size of the graphite and the good adherence of the binder on the graphite surface. An important advantage of a mixed SBR and Na-CMC binder is the good stability for the nano-silicon/graphite (TIMREX® KS6 and SP) electrode with the use of significantly less binder material. As low as 1–2% of SBR mixed with 1–2% Na-CMC as a binder is sufficient to assure a good electrochemical performance of nano-silicon/graphite electrodes. Another advantage is the potentially lower process cost of these environmentally benign binders: Na-CMC can be dissolved and processed in water and SBR in ethyl acetate, respectively instead of NMP. An important result is that the

content of SBR and SBR/Na-CMC mixtures should be kept at maximum of 5–6%, because larger amounts of SBR and Na-CMC lead to a barrier formation, which obviously hinders the Li^+ -diffusion and deteriorates the performance of the electrodes upon cycling.

Acknowledgements

The authors would like to express their gratitude to Dr. Michael E. Spahr (TIMCAL SA, Bodio, Switzerland) for the donation of the graphite samples, Selectchemie AG (Zürich, Switzerland) for the donation of methyl cellulose and ethyl cellulose samples, Dow Chemicals (Dow Chemicals, Horgen, Switzerland) for the donation of the SBR sample and Mr. Laurence J. Hardwick for the editing of this article.

References

- [1] M. Broussely, *J. Power Sources* 81–82 (1999) 140.
- [2] A.N. Jansen, A.J. Kahaian, K.D. Kepler, P.A. Nelson, K. Amine, D.W. Dees, D.R. Vissers, M.M. Thackeray, *J. Power Sources* 81–82 (1999) 902.
- [3] X. Zhang, P.N. Ross Jr., R. Kostecki, F. Kong, S. Sloop, J.B. Kerr, K. Striebel, E.J. Cairns, F. McLarnon, *J. Electrochem. Soc.* 148 (2001) A463.
- [4] S.S. Zhang, T.R. Jow, *J. Power Sources* 109 (1999) 422.
- [5] J. Drogenik, M. Gaberscek, R. Dominko, F.W. Poulsen, M. Mogensen, S. Pejovnik, J. Jamnik, *Electrochim. Acta* 48 (2003) 883.
- [6] D. Guy, B. Lestriez, R. Bouchet, V. Gaudefroy, D. Gyomard, *Electrochem. Solid-State Lett.* 8 (2005) A17.
- [7] W. Liu, M. Yang, H. Wu, S.M. Chiao, N. Wu, *Electrochem. Solid-State Lett.* 8 (2005) A100.
- [8] J.O. Besenhard, J. Yang, M. Winter, *J. Power Sources* 68 (1997) 87.
- [9] A.M. Wilson, J.R. Dahn, *J. Electrochem. Soc.* 142 (1995) 326.
- [10] M. Yoshio, S. Kugino, N. Dimov, *J. Power Sources* 153 (2006) 375.
- [11] M. Wachtler, M.R. Wagner, M. Schmied, M. Winter, J.O. Besenhard, *J. Electroanal. Chem.* 510 (2001) 12.
- [12] Z. Chen, L. Christensen, J.R. Dahn, *J. Electrochem. Soc.* 150 (2003) A1073.
- [13] J.H. Lee, S. Lee, U. Paik, Y.M. Choi, *J. Power Sources* 147 (2005) 249.
- [14] H. Buqa, A. Würsig, D. Goers, L.J. Hardwick, M. Holzapfel, F. Krumeich, M.E. Spahr, P. Novák, *J. Power Sources* 146 (2005) 134.
- [15] E. Deiss, D. Häring, P. Novák, O. Haas, *Electrochim. Acta* 46 (2001) 4185.
- [16] H. Buqa, D. Goers, M. Holzapfel, M.E. Spahr, P. Novák, *J. Electrochem. Soc.* 152 (2005) A474.
- [17] M. Holzapfel, H. Buqa, W. Scheifele, P. Novák, F. Petrat, *Chem. Commun.* 12 (2005) 1566.