

Impact of co-solvent chain branching on lithium-ion battery performance

Jens Vetter, Hilmi Buqa, Michael Holzapfel, Petr Novák*

Electrochemistry Laboratory, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland

Available online 27 April 2005

Abstract

The influence of the electrolyte in lithium-ion batteries on the reversible capacity and long-term cycling stability is not only determined by the salt and the film-forming solvent, but also, to a minor extent, by the co-solvent that is usually comprised in order to ensure suitable physical properties. Electrolytes containing three different isomers of butyl methyl carbonates were investigated in both, graphite half- and full-cells in order to determine the influence of co-solvent chain branching on the electrochemical performance. The reversible capacity obtained in SFG44 graphite (TIMCAL Ltd.) half-cells is higher for electrolytes with branched co-solvents and increases as the chain branching gets closer to the carbonate group. The long-term cycling stability, investigated in SLP30 graphite (TIMCAL Ltd.) half-cells, shows the same trend. The overall effect is rather small, but still perceivable in a full-cell set-up (SFG44/LiCoO₂). A possible pathway of interaction of the co-solvent via the structure and composition of the solid electrolyte interphase (SEI) is proposed.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Lithium-ion batteries; Electrolyte; Solvent; Branched isomer; Cycling stability; Electrochemical performance

1. Introduction

Organic carbonates are widely used as solvents in state-of-the-art lithium-ion batteries. Many compounds have been tested as solvents over the years but, since only a few compounds are commercially available, systematic fundamental investigations have seldom been made [1–4]. The influence of various solvent parameters on battery performance is hardly understood. Performance is determined to a major part by the film-forming solvent component and the electrolyte salt. So far, little attention has been paid to the co-solvent. In a recent publication we reported on the influence of chain length in alkyl methyl carbonate co-solvents on the electrochemistry of graphite anodes [5]. During these studies we proved the suitability of *n*-alkyl methyl carbonates as co-solvents in lithium-ion battery electrolytes. In this paper, in order to further understand the influence of the co-solvent parameters, we focused our attention on chain-branching. *n*-Butyl methyl carbonate (BMC) showed a reasonable performance in previous studies. Additionally its isomers *iso*-butyl methyl

carbonate (*i*BMC) and *sec*-butyl methyl carbonate (*s*BMC) were also chosen for a comparative study of cell performance.

2. Experimental

BMC, *i*BMC, and *s*BMC were synthesized in-house as described previously [5] and purified by distillation to a purity of >99.5% (GC). Ethylene carbonate (EC), dimethyl carbonate (DMC), and LiPF₆, as well as the reference electrolyte EC/DMC 1:1 (w/w), 1 M LiPF₆, were commercial battery grade products and used as received.

Electrochemical cycling experiments were performed using 1 M LiPF₆ solutions in different solvent mixtures. The experiments were carried out in both, graphite half-cells with metallic lithium as the counter and reference electrode, and in full-cell set-up using graphite and LiCoO₂ electrodes as the anode and cathode, respectively. Two types of graphite were used as the working electrode in the half-cell setup. The electrodes were prepared in-house by a doctor-blading method. The cells were assembled in an argon-filled glove box at a moisture and oxygen level below 5 ppm. The elec-

* Corresponding author. Tel.: +41 56 310 2457; fax: +41 56 310 4415.
E-mail address: petr.novak@psi.ch (P. Novák).

trochemical experiments were performed at $25(\pm 0.1)^\circ\text{C}$. The charge/discharge rate for the half-cell experiments was $C/30$ in the first cycle and $C/5$ in the subsequent cycles, based on graphite active mass. The full-cells were cycled at $C/10$ in the first cycle and $C/2$ in the subsequent cycles, the rate based on oxide active mass. During the intercalation/charge half cycle, a CCCV procedure was applied to ensure complete lithium intercalation into the graphite.

3. Results and discussion

In half-cells with TIMREX[®] SFG44 graphite (TIMCAL Ltd.) and EC/DMC, 1M LiPF₆ electrolytes, typically, a reversible charge capacity of ca. 340 Ah kg^{-1} (of carbon) is observed instead of the theoretical maximum value of 372 Ah kg^{-1} . This is usually explained by the large particle size and a slow kinetics of the lithium migration in the graphite [6,7]. But our experiments with different electrolytes give hints that there are also other, electrolyte related parameters that influence the reversible capacity. If DMC is substituted by the BMC isomers, a reversible charge capacity of $350\text{--}360\text{ Ah kg}^{-1}$ can be achieved, showing that the choice of electrolyte has a significant impact.

As can be seen from Fig. 1, the reversible (specific) capacity of half-cells with SFG44 graphite increases in the series $\text{DMC} < i\text{BMC} < \text{BMC} \cong s\text{BMC}$. Fig. 1 illustrates the charge

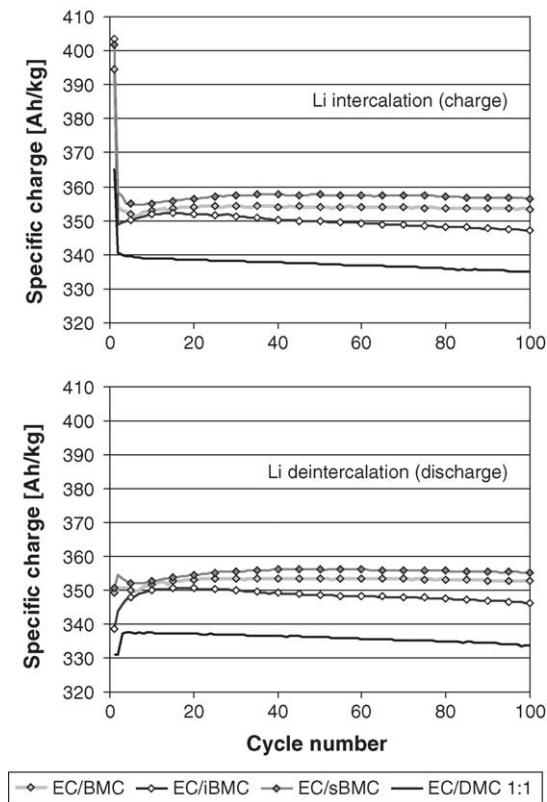


Fig. 1. Specific charge capacity in SFG44 half cells vs. metallic Li with isomeric BMC electrolytes (1:2 mixtures) containing 1 M LiPF₆.

and discharge capacities for the 1:2 (w/w) mixtures. The results for the 1:1 mixtures reveal the same trend but are not presented here, since all the cells show a specific capacity greater than 350 Ah kg^{-1} (per mass of carbon) during the first 100 cycles, and more than 99% of the specific capacity in the second cycle is retained in the 100th cycle. With values as close together as this, investigations on differences of behavior are hardly possible in consideration of the measurement errors.

The same mechanisms that enhance the reversible specific capacity are expected to have an impact on cycleability, too. Since the long-term fading behavior of SFG44 is excellent, regardless of the electrolyte used, differences can hardly be investigated using this graphite. In order to obtain a better estimation of the long-term behavior of cells with the BMC isomers, TIMREX[®] SLP30 graphite (TIMCAL Ltd.) was used. Compared to SFG44, SLP30 has a rounded particle shape. Without the use of an additive, we found slightly reduced cycling stability of SLP30 electrodes in EC/DMC electrolytes. With this graphite, the effects of chain branching on cycleability become more obvious.

For 1 M LiPF₆, 1:1 (w/w) mixtures of EC with the BMC isomers, some differences in the cycling stability of half-cells with SLP30 can be observed (Fig. 2). In order to eliminate possible weighing errors, apart from the absolute values for the specific charge capacity, the relative specific

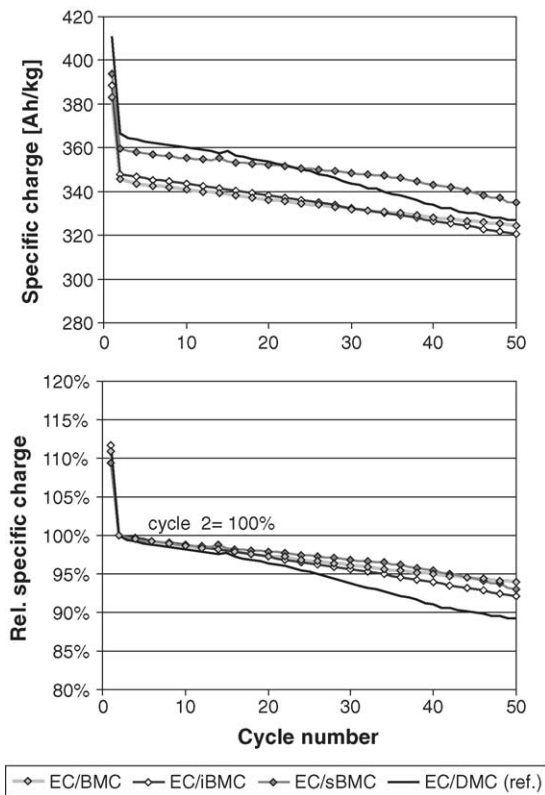


Fig. 2. Relative (bottom) and absolute (top) cycling behavior (Li intercalation) in SLP30 half cells vs. metallic Li with isomeric BMC electrolytes (1:1 mixtures) containing 1 M LiPF₆.

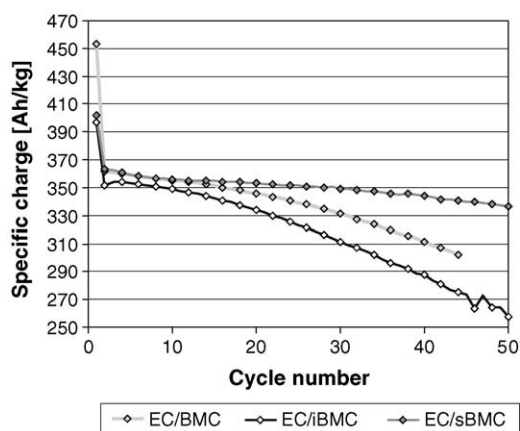


Fig. 3. Cycling behavior (Li intercalation) in SLP30 half cells vs. metallic Li with isomeric BMC electrolytes (1:2 mixtures) containing 1 M LiPF₆.

charge capacity compared to the second cycle is given in Fig. 2 (bottom). The cycling stability increases in the order *i*BMC < BMC < *s*BMC and, in the case of *s*BMC, it even outperforms the reference EC/DMC. Differences in cycling behavior become more prominent if the portion of the co-solvent in the electrolyte is increased. For 1:2 mixtures of EC with the BMC isomers, large differences can be observed (Fig. 3). Again, the cycling stability increases in the same order as for the 1:1 mixtures. EC/*s*BMC 1:2 also outperforms our reference electrolyte EC/DMC 1:1, as it is the case for EC/*s*BMC 1:1.

One possible explanation for the increased reversible capacity would be a higher ionic conductivity in the electrolytes comprising the BMC isomers, but EC/DMC shows the highest conductivity of the electrolytes tested (Table 1), ruling out electrolyte conductivity as the main influence. Another, more probable, interaction pathway of the electrolyte is by influencing the properties of the solid electrolyte interphase (SEI). The SEI is a passivating film formed from electrolyte reduction products on the carbon electrode during the initial charge/discharge cycles. It is electronically insulating but allows the passage of lithium ions. This protects the electrolyte from further reduction and the (charged) electrode from corrosion, and, at the same time, ensures the proper function of the battery. The SEI is described as a network of interpenetrating organic and inorganic layers [8–10], formed from decomposition products of both, the conducting salt, and the organic solvent mixture. It is commonly accepted that EC plays a major role in the formation of a stable SEI [10–13]. The influence of the co-solvent on the SEI, on the other hand,

is usually considered as minor. The co-solvent is usually understood as a “thinner”, lowering both, the electrolyte viscosity and melting point but having little influence on chemical transformations in the battery. Nevertheless, the results presented here can be explained best by assuming an influence of the co-solvent on the formation of the SEI. It is widely accepted that the organic component of the SEI is of polymeric nature. The co-solvent may have an impact on the structure and properties of the SEI either indirectly by guiding the reduction and polymerization mechanisms, or directly by decomposition of the co-solvent and incorporation of the reduction products into the SEI. Both pathways lead to an SEI film with slightly modified properties and electrochemical behavior.

The modifications of the SEI by different co-solvents are only minor for two reasons. First, the main film-forming compound, EC, remains the same, since it is reduced much easier than any of the co-solvents in this study [14]. In our experiments, this can be deduced from the good cycling performance, since protective films formed from acyclic carbonates are known to be instable and lead to comparatively high fading rates [1]. Second, the chemical properties of the acyclic carbonate co-solvents are dominated by the carbonate group, and the influence of different alkyl groups on reactivity is small, especially if isomeric groups are considered. Although the BMC isomers can be expected to react quite similarly, the different spatial demand of alkyl groups may influence the structure and properties of the reaction products, especially if incorporated in an ion conducting polymer as the SEI. Even if present in small numbers only, spatially demanding groups may disturb the order in a polymeric compound and significantly influence ion transport properties. For that reason, we favor the second interaction pathway, the incorporation of decomposition products of the co-solvent in the SEI, as an explanation of our results.

The positive results in half-cells encouraged us to investigate the cycling behavior of the BMC isomer electrolytes in full-cells. To obtain more easily distinguishable results, the more challenging 1:2 electrolyte mixtures were chosen for the experiments. As anode and cathode active material we chose the more stable graphite SFG44 and LiCoO₂, respectively. The electrodes were balanced to be cathode limited with a slight excess (ca. 7%) of anode material, i.e., the cell capacity is determined by the cathode capacity. Therefore, the differences in reversible capacity of the graphite in different electrolytes do not influence the overall cell capacity. Thus, the only influence of the electrolyte should be on capacity fading and cycling stability. Unexpectedly, the reversible capacity obtained in the full-cell set-up varied with different electrolyte solutions (Fig. 4). The type of electrolyte used, of course, has also an impact on the rate capability of the cells due to differences in conductivity. Obviously, this also affects the reversible charge capacity obtained in our experiments. This is most probably due to an incomplete discharge of the cell, since a CCCV profile was used only during the charging of the cell, while the discharge half-cycle was performed at

Table 1
Conductivity of 1:1 (w/w) electrolyte solutions containing 1 M LiPF₆

	Conductivity (mS cm ⁻¹)
EC/DMC	11.7
EC/BMC	≈5.9 ^a
EC/ <i>i</i> BMC	≈5.4 ^a
EC/ <i>s</i> BMC	≈6.5 ^a

^a Experimental error, ca. ±0.5 mS cm⁻¹.

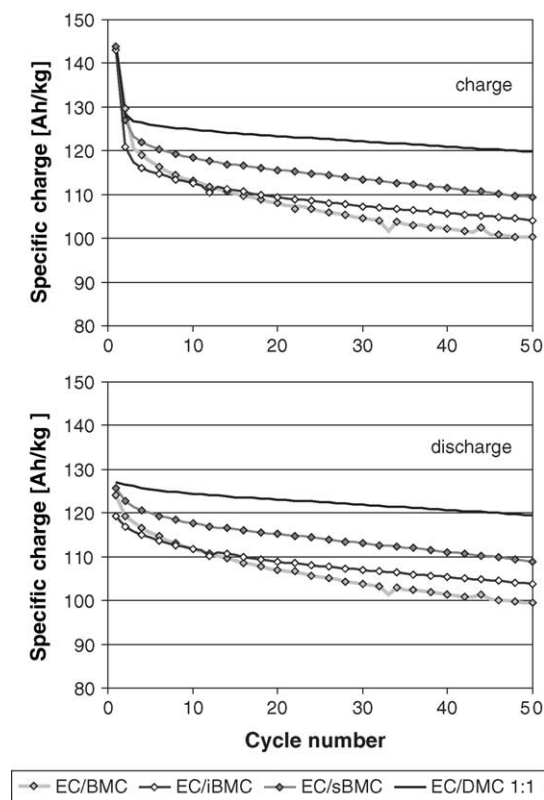


Fig. 4. Cycling behavior in SFG44–LiCoO₂ full-cells with isomeric BMC electrolytes (1:2 mixtures) containing 1 M LiPF₆. The specific charge relates to cathode active mass.

a constant current rate of $C/2$. (This charge-discharge profile most closely resembles the procedures used in a real battery.) The assumption of the incomplete discharge is supported by the fact that a large part of the “lost” capacity can be recovered by applying a CCCV profile in the discharge half-cycle, too.

Apart from the lower reversible charge capacity, a slightly increased capacity fading could be observed. This finding differs from our results in graphite half-cells versus metallic lithium, indicating some process(es) occurring at the cathode. The initial reversible capacity found in the experiments, on the whole, follows the electrolyte conductivity, i.e. the order $iBMC < BMC < sBMC$, which is the same as for the cycling stability in half-cells. In terms of cycling stability, on the other hand, the BMC electrolyte shows a somewhat higher fading, as can be seen in Fig. 5, whereas the fading is practically identical for the $iBMC$ and $sBMC$ electrolytes, although not quite as low as for our reference electrolyte EC/DMC 1:1. It should be mentioned here that the electrolyte mixtures used for this study are not optimized in any way, and that the impurities in the BMC isomers are neither specially controlled nor analyzed, except for their total content which is below 0.5% in the pure solvent. Therefore, it is reasonable to assume that for optimized electrolyte mixtures and controlled purity the performance might be enhanced to a level at least comparable to the reference electrolyte.

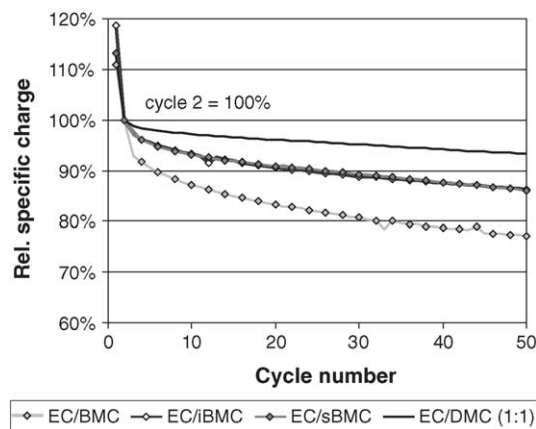


Fig. 5. Relative cycling behavior (charge half-cycle) in SFG44–LiCoO₂ full-cells with isomeric BMC electrolytes (1:2 mixtures) containing 1 M LiPF₆.

4. Conclusions

Chain branching of the electrolyte co-solvent has an influence on both reversible capacity and long-term cycling behavior. The mechanism is not yet clear, but the most probable pathway is via the solid electrolyte interphase (SEI). It seems that chain branching close to the carbonate group (as in $sBMC$) has a positive effect on the reversible capacity and fading in graphite half-cells. The influence of chain branching at a site remote from the carbonate group (as in $iBMC$) is weaker and seems to vary with different types of graphite. In a full-cell set-up, the effect of chain-branching is less clear at the present, but it seems that in this case, also, the cycling stability increases as the chain branching gets closer to the carbonate group. In summary, the influence of co-solvent chain branching is small but perceivable, and seems to be mainly beneficial for cycling stability.

Acknowledgment

The authors would like to thank the TIMCAL Group, Bodio, Switzerland, namely Dr. Michael E. Spahr, for supply of graphite materials and valuable discussions.

References

- [1] Y. Ein-Eli, S.F. McDevitt, R. Laura, J. Electrochem. Soc. 145 (1998) L1–L3.
- [2] Y. Ein-Eli, S.F. McDevitt, R. Laura, Proc. Power Sources Conf. 38 (1998) 448–451.
- [3] Y. Ein-Eli, S.F. McDevitt, C. Wu, R. Laura, Proc. Electrochem. Soc. 98–16 (1999) 416–422.
- [4] G.C. Chung, H.J. Kim, S.I. Yu, S.H. Jun, J.W. Choi, M.H. Kim, J. Electrochem. Soc. 147 (2000) 4391–4398.
- [5] J. Vetter, P. Novak, J. Power Sources 119–121 (2003) 338–342.
- [6] D. Aurbach, B. Markovsky, A. Shechter, Y. Ein Eli, H. Cohen, J. Electrochem. Soc. 143 (1996) 3809–3820.
- [7] K. Zaghbi, X. Song, A. Guerfi, R. Kostecki, K. Kinoshita, J. Power Sources 124 (2003) 505–512.

- [8] E. Peled, D. Bar Tow, A. Merson, A. Gladkich, L. Burstein, D. Golodnitsky, *J. Power Sources* 97–98 (2001) 52–57.
- [9] E. Peled, D. Golodnitsky, G. Ardel, *J. Electrochem. Soc.* 144 (1997) L208–L210.
- [10] M. Winter, J.O. Besenhard, M.E. Spahr, P. Novak, *Adv. Mater.* 10 (1998) 725–763.
- [11] E. Peled, D. Golodnitsky, J. Penciner, in: J.O. Besenhard (Ed.), *Handb. Battery Mater.*, Wiley-VCH, Weinheim, Germany, 1999, pp. 419–456.
- [12] J.R. Dahn, A.K. Sleight, H. Shi, B.M. Way, W.J. Weydanz, J.N. Reimers, Q. Zhong, U. von Sacken, in: G. Pistoia (Ed.), *Lithium Batteries—New Materials, Developments and Perspectives*, Elsevier, Amsterdam, 1994, pp. 1–47.
- [13] R. Fong, U. Vonsacken, J.R. Dahn, *J. Electrochem. Soc.* 137 (1990) 2009–2013.
- [14] R. Mogi, M. Inaba, Y. Iriyama, T. Abe, Z. Ogumi, *J. Power Sources* 119 (2003) 597–603.