

# Novel alkyl methyl carbonate solvents for lithium-ion batteries

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## Abstract

Electrochemical cycling tests on cells with graphite electrodes and several alkyl methyl carbonates were performed. Experiments with single solvent electrolytes and binary mixtures with ethylene carbonate (EC) showed that the alkyl methyl carbonates  $\text{H}_3\text{CO}(\text{CO})\text{O}(\text{CH}_2)_n\text{H}$  ( $n = 3\text{--}5$ ) are suitable as co-solvents in lithium-ion batteries. Butyl methyl carbonate (BMC) showed the best performance in these experiments. Ternary mixtures of EC, BMC, and propylene carbonate (PC) allow cycling of cells with a graphite anode material that is otherwise incompatible with EC/PC electrolytes. This is probably because BMC-based electrolytes form the solid electrolyte interphase (SEI) at more positive potential than electrolytes based on PC.

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## 1. Introduction

State-of-the-art lithium-ion batteries consist of a carbon-based negative electrode, a positive lithium metal mixed oxide electrode, and a separator soaked in an organic electrolyte. The electrolyte is usually composed of a lithium salt dissolved in an organic solvent mixture. Among the solvents used is a variety of cyclic and non-cyclic carbonates, namely, ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC). Since these solvents are not thermodynamically stable at the potential of metallic lithium or lithiated carbon, they decompose during the first charge/discharge cycles. On the surface of the negative electrode, they form an electrically insulating, lithium-ion conducting protective film, called the solid electrolyte interphase (SEI). The stability of the SEI is essential for safe and effective working of the whole battery. Since the formation of the SEI is associated with irreversible charge consumption, which lowers the usable charge density of the cell, a quick and charge-effective formation, along with a good long-term stability of the SEI is desirable.

Since the SEI is build up of decomposition products of the electrolyte, the performance of the cell depends to a great extent on the composition of the electrolyte solution and the electrochemical behavior of every single electrolyte component. Nevertheless, since only a few of the compounds of

interest are commercially available, systematic investigations on the topic have seldom been made.

In this paper we report on a systematic study of the electrochemical behavior of some compounds of the homologous series of the alkyl methyl carbonates interesting for lithium-ion batteries, both as single solvents and co-solvents in binary and ternary mixtures with EC and PC. Electrochemical cycling experiments have been performed to compare the first cycle irreversible charge capacity and long-term cycling stability of graphite electrodes in these various electrolytes.

## 2. Experimental

The organic carbonates butyl methyl carbonate (BMC) and methyl pentyl carbonate (MPentC) were synthesized by the reaction of the corresponding alcohol with methyl chloroformate in the presence of pyridine and dichloromethane as the solvent. After purification by filtration, washing with water, and column distillation, the pure compounds were obtained in high yield and sufficient purity (>99.5% GC). Methyl propyl carbonate (MPC), EC, and PC were supplied by Merck KGaA (Darmstadt, Germany, Selectipure<sup>®</sup>) and used as delivered.

The experiments were performed at 25 °C under strict temperature control using 1 M  $\text{LiClO}_4$  (Merck) solutions unless otherwise indicated. The water content of the electrolytes as determined by Karl–Fischer titration was less than 10 ppm.

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Galvanostatic cycling experiments were performed in laboratory test cells with a coin-cell-type design [1] and an electrode area of  $1.33 \text{ cm}^2$ . Graphite electrodes (UF8, Graphitwerk Kropfmühl AG, Hauzenberg, Germany, and TIMREX<sup>®</sup> SLP30, TIMCAL SA, Bodio, Switzerland) were prepared as described elsewhere [2,3]. Cells containing the graphite electrode, an electrolyte-soaked glass fibre separator, and a lithium metal counter electrode were assembled in an argon filled glove box having an oxygen and water content of less than 5 ppm. The lithium counter electrode served also as a reference electrode against which all potentials throughout the paper are given. The cells were cycled on a BATSMAL battery measurement system (Astrol Electronic AG, Baden-Dättwil, Switzerland). Cycling rates of  $C/30$  and  $C/10$  in the first cycle and  $C/7$  and  $C/10$ , respectively, in the following cycles were used at 100% DOD. Therefore, most of the irreversible charge consumption (“charge loss”) occurred during the first cycle, which was performed galvanostatically between 1.5 V and 5 mV. In the intercalation half-cycle, at 5 mV the current was lowered potentiostatically to  $C/50$  (constant current constant voltage (CCCV) charging as usual for commercial batteries). The irreversible charge consumption is defined as the difference between the cathodic and anodic charge of the cycle, given in percent relative to the total cathodic charge ( $\text{Li}^+$  insertion) of the cycle.

### 3. Results

For a given graphite and salt, the quality of the SEI formed during the first cycles depends mainly on the composition of the solvent mixture and its electrochemical behavior. EC is known as a good film-forming compound, while PC, e.g. shows a rather poor behavior, especially with most synthetic graphites in the carbon electrode. Unfortunately, EC cannot be used as a single solvent for room temperature applications due to its high freezing point of  $36^\circ\text{C}$ . It has to be mixed with some co-solvents to ensure sufficient low-temperature electrolyte conductivity. Among the co-solvents tested for the purpose, non-cyclic organic carbonates have shown the best performance to date. Ein-Eli et al. [4] found asymmetric alkyl methyl carbonates to be superior to alkyl ethyl carbonates when used as single solvents in lithium-ion batteries. Therefore, we chose the carbonates of the general formula  $\text{H}_3\text{CO}(\text{CO})\text{O}(\text{CH}_2)_n\text{H}$  ( $n = 3-5$ ) for our investigations.

#### 3.1. Single solvents

In accordance with earlier results [4], rather high first cycle irreversible charge capacities are obtained with the non-cyclic carbonates as single solvents. With the natural graphite UF8 they reach a maximum for BMC ( $n = 4$ ), which shows an irreversible charge capacity (throughout the technical literature called “charge loss”) of 42%, while MPC ( $n = 3$ ) and MPentC ( $n = 5$ ) exhibit losses of 27 and 29%, respectively. After the first ten cycles the rever-

sible charge capacity of the latter two drops from an initial value of 350 Ah/kg to below 50 Ah/kg, whereas BMC still has a reversible capacity of 280 Ah/kg. The lithium intercalation occurs mostly during the potentiostatic charging phase, indicating high internal cell resistance, possibly due to a low ionic conductivity of the SEI. It should be mentioned that these findings for  $\text{LiClO}_4$ -based electrolytes differ from published results obtained with 1 M  $\text{LiPF}_6$  as the conducting salt [4], in which only small declines in reversible charge capacities are reported.

#### 3.2. Binary solvent mixtures

To diminish charge losses and improve cycling stability, various binary mixtures of the non-cyclic carbonates with EC were investigated to find the best carbonate and an optimum composition. Mixtures with an EC content of 50, 40, and 20 wt.% and 1 M  $\text{LiClO}_4$  as the conducting salt were tested. The results are shown in Fig. 1 and summarized in Table 1. Data are also given for EC/DEC mixtures as a reference. It can be seen that, mixtures of MPC and MPentC with EC, as is the case for the single solvents, build up high internal resistances leading to slow lithium insertion into the graphite. Fig. 1 gives the cycling data normalized to the second cycle to eliminate differences in first cycle charge losses. Since all 1:1 mixtures behave virtually the same in this graph, data are shown for lower EC content only. In mixtures containing BMC, as for DEC, sufficiently high reversible capacities can be obtained even after prolonged cycling (above 340 Ah/kg after 100 cycles), whereas a slow capacity fading is observed for both MPC and MPentC. Furthermore, while the mixed solvent EC/DEC 1:4 exhibits rapid capacity fading leading to premature cell death after only a few cycles (Fig. 1, inset), both EC/BMC mixtures, 1:4 and 2:3 by weight, show high reversible capacities.

#### 3.3. Ternary solvent mixtures

Based on the higher cycling rates in binary mixtures, BMC was chosen for further examination in ternary mix-

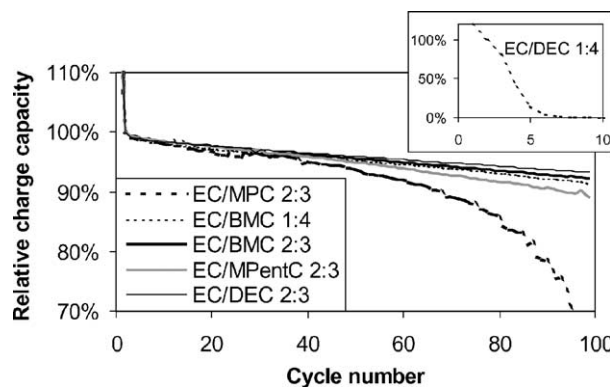


Fig. 1. Cycling behavior of graphite electrodes in cells with alkyl methyl carbonate/EC mixtures (1 M  $\text{LiClO}_4$ , UF8 vs. Li metal).

Table 1

First cycle charge losses and cycling behavior of graphite electrodes in binary mixtures of alkyl methyl carbonates with EC (1 M LiClO<sub>4</sub>, UF8 vs. Li metal)

Ratio (% EC)	EC/DEC		EC/MPC		EC/BMC		EC/MPentC	
	Cycles <sup>a</sup>	Charge loss (%)	Cycles <sup>a</sup>	Charge loss (%)	Cycles <sup>a</sup>	Charge loss (%)	Cycles <sup>a</sup>	Charge loss (%)
1:1 (50)	>100	16.5	≈70 <sup>b</sup>	17.2 <sup>b</sup>	>100	18.2	>100 <sup>c</sup>	16.2 <sup>c</sup>
2:3 (40)	>100	16.0	≈100 <sup>b</sup>	14.8 <sup>b</sup>	>100	18.7	>100 <sup>b</sup>	18.0 <sup>b</sup>
1:4 (20)	<5	16.4	≈50 <sup>b</sup>	12.8 <sup>b</sup>	≈100 <sup>d</sup>	20.4 <sup>d</sup>	>50 <sup>e</sup>	17.4 <sup>e</sup>

<sup>a</sup> Number of cycles until the reversible charge capacity drops below 80% of its original value.<sup>b</sup> Rate decreases after 30 cycles.<sup>c</sup> Rate decreases at the end.<sup>d</sup> Rate decreases after 45 cycles.<sup>e</sup> Low insertion rate.

Table 2

First cycle charge losses of graphite electrodes in EC/PC/BMC mixtures (1 M LiClO<sub>4</sub>, natural UF8 or synthetic SLP30 graphite vs. Li metal)

Electrolyte			Charge loss		
	EC/PC/BMC	wt.% EC	wt.% PC	UF8 (%)	SLP30 (%)
1:0:4	20	0	20.4	13.7	
1:2:1	25	50	16.8	38.3	
2:3:3	25	37.5	16.1	21.2	
1:1:2	25	25	17.4	13.6	
1:1:1	33	33	16.6	19.4	
2:3:0	40	60	21.1	Incompatible, exfoliation	
2:2:1	40	40	16.1	27.7	
4:3:3	40	30	16.4	16.2	
2:1:2	40	20	16.9	11.9	
2:0:3	40	0	18.0	13.1	

tures with EC and PC. PC is widely utilized as organic solvent in lithium batteries due to its wide electrochemical stability window and good compatibility with cathode materials. Nevertheless, it causes serious problems in secondary cells if graphite is used as the anode material due to exfoliation of the graphite. This process leads to a high charge loss during the first charge/discharge cycles and enhanced capacity fading upon prolonged cycling. In many tailored synthetic graphites, exfoliation even dominates over SEI film formation and prohibits cycling completely [5–7]. To minimize these problems, binary mixtures with EC are commonly used. Total or partial substitution of PC by other co-solvents, e.g. *trans*-2,3-butylene carbonate [8,9], diminishes exfoliation and allows the use of synthetic graphites as anode materials in lithium-ion batteries.

To evaluate the suitability of BMC as a substitute for PC, we carried out a series of electrochemical cycling experiments with various ternary mixtures of EC, PC, and BMC, using both natural and synthetic graphites as intercalation electrodes. Table 2 summarizes the first cycle charge losses observed in these experiments.

Using natural graphite UF8 as intercalation material, for both EC/BMC 2:3 and all ternary EC/PC/BMC mixtures, first cycle charge losses are significantly lower than for EC/PC 2:3 (Table 2, Fig. 2). Despite slightly higher fading rates

in the subsequent cycles, the BMC containing mixtures still outperform EC/PC 2:3 in terms of overall charge capacity during the first 100 cycles (Fig. 2).

With the synthetic SLP30 graphite, which cannot be cycled in EC/PC 2:3 due to excessive exfoliation, ternary mixtures show a clear relation between PC content and relative charge capacity (Fig. 3). First cycle charge losses also strongly depend on PC content, as can be seen from Table 2. Astonishingly some ternary mixtures even outper-

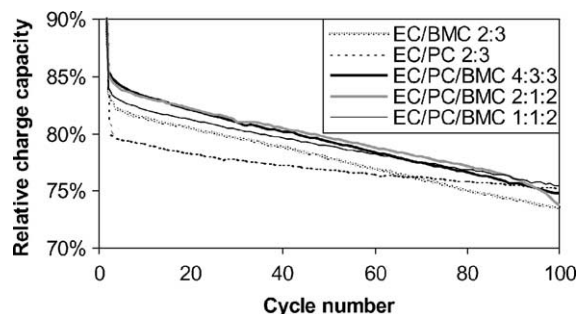


Fig. 2. Cycling behavior (intercalation half-cycle) of graphite electrodes in various binary and ternary EC/PC/BMC mixtures (40% EC content), normalized to the first cycle charge capacity (1 M LiClO<sub>4</sub>, UF8 vs. Li metal).

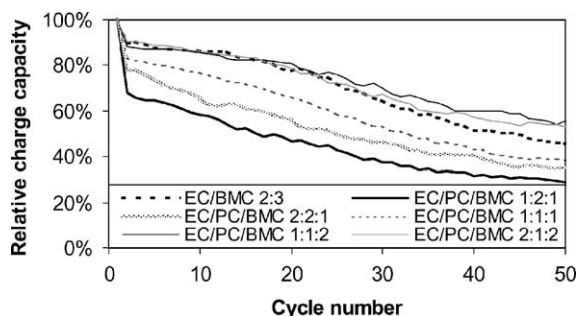


Fig. 3. Cycling behavior (intercalation half-cycle) of graphite electrodes in various binary and ternary EC/PC/BMC mixtures, normalized to the first cycle charge capacity (1 M LiClO<sub>4</sub>, SPL30 vs. Li metal).

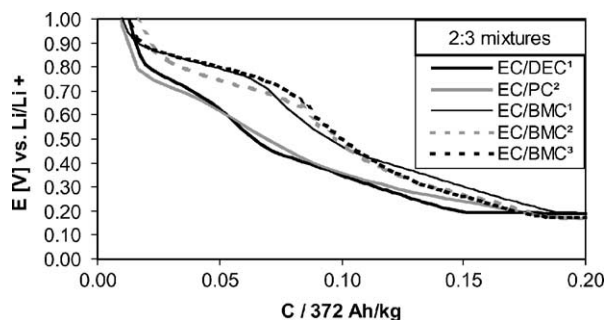


Fig. 5. Magnification of the formation region of the first galvanostatic charge/discharge cycle for various electrolytes (UF8 vs. Li metal). For annotations see Fig. 4.

form EC/BMC 2:3. This is particularly the case for mixtures with a low EC content.

#### 4. Discussion

Among the alkyl methyl carbonates MPC, BMC, and MPentC, mixtures containing BMC as a co-solvent together with EC as a film-forming agent show the best cycling performance. This is true for first cycle charge losses as well as for long-term cycling behavior. Since changes in later cycles are limited, investigations are preferably done over the first (i.e. formation) cycle. During SEI formation, effects that are undetectably small in the later cycles are still considerable. In the charging curves of the first cycle, a substantial difference is visible between electrolytes containing BMC and the ones without. Fig. 4 compares the first cycle behavior of various electrolytes. A magnification of the formation region is given in Fig. 5. The curves in Figs. 4 and 5 are normalized to 372 Ah/kg, the theoretical charge capacity of graphite according to the formula LiC<sub>6</sub>. It is obvious that side reactions, especially the SEI formation, are not completed in the first cycle because the charge loss does not reach its final value before 40 cycles (Fig. 6). Therefore, normalization has also been done by extrapolating a hypothetical first cycle charge capacity by linear regression

of the charge capacity of cycles 40–80. Nevertheless, since the results of the calculation were much the same, the original data are depicted.

Major differences are obvious in the magnification of the formation region (Fig. 5). With BMC containing electrolytes, decomposition starts at a potential of approximately 0.9 V versus Li/Li<sup>+</sup>, while decomposition of electrolytes based on DEC or PC as the co-solvent for EC begins at 0.8 V. Anyway, the overall charge capacity is roughly the same for all assessed mixtures (Fig. 4). This means that, despite an earlier onset of decomposition, the overall charge

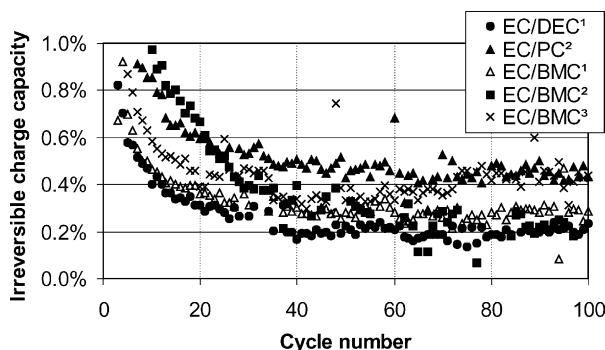


Fig. 6. Irreversible charge capacities (charge losses) for binary solvent mixtures (2:3, 1 M LiClO<sub>4</sub>, UF8 vs. Li metal). For annotations see Fig. 4.

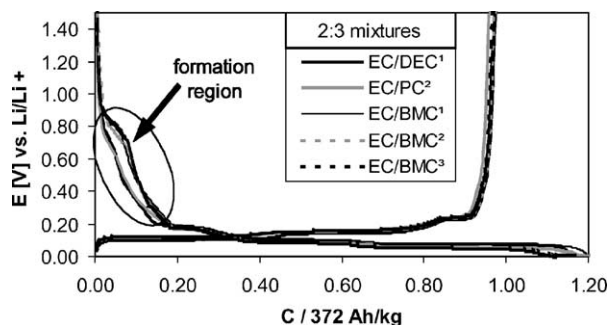


Fig. 4. First galvanostatic charge/discharge cycle for various electrolyte mixtures (UF8 vs. Li metal): (1) 1 M LiClO<sub>4</sub>, C/30; (2) 1 M LiClO<sub>4</sub>, C/10; (3) 1 M LiPF<sub>6</sub>, C/10.

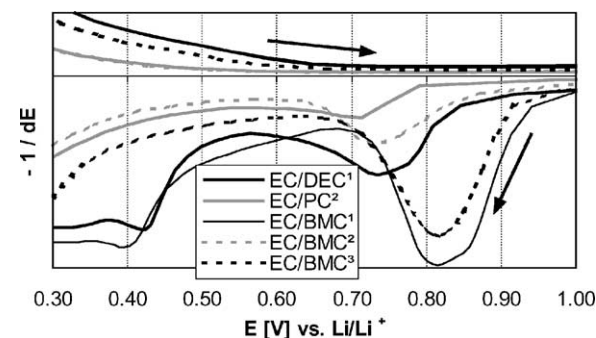


Fig. 7. Derivation of the potential during the first galvanostatic cycle of graphite electrodes in various electrolytes (2:3, 1 M LiClO<sub>4</sub>, UF8 vs. Li metal). For annotations see Fig. 4.

loss is the same, and in consequence, the SEI formation is complete more quickly. This more rapid formation is also indicated by the steeper (negative) slope of the curves of BMC-based electrolytes compared to PC- and DEC-based ones (Fig. 5), and by the derivation of the potential during the first cycle (Fig. 7). Since the curves indicate the overlap of at least two electrochemical processes, SEI film formation and lithium intercalation, it can be supposed, that the two processes are separated more distinctly in the BMC case.

## 5. Conclusions

The alkyl methyl carbonates MPC, BMC, and MPentC are suitable as co-solvents in lithium-ion batteries with graphitized carbon as the negative electrode active material. These carbonates can be used as substitutes for DEC or PC. Best results are obtained using mixtures containing BMC. In binary mixtures of BMC, it is possible to use lower EC contents than is the case with DEC or PC as the co-solvent. Ternary mixtures of EC, PC, and BMC show decreased first cycle charge losses and increased reversible charge capacity compared to EC/PC. Reversible capacities obtained with ternary mixtures can exceed the ones with either of the binary mixtures EC/PC and EC/DEC.

Although the reasons for the differences in behavior of the co-solvents are not fully understood yet and further investigations are necessary, a vast field for future improvements is now open.

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