



Methyl tetrafluoro-2-(methoxy) propionate as co-solvent for propylene carbonate-based electrolytes for lithium-ion batteries

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ABSTRACT

Methyl tetrafluoro-2-(methoxy) propionate (MTFMP) was evaluated as co-solvent for PC-based electrolytes in combination with graphite electrodes. Already 10 wt% (5.6 mol%) of MTFMP in PC were sufficient to form an effective and stable SEI on graphite as confirmed by battery tests. In the first cycle, the formation of an effective SEI via the decomposition of MTFMP was observed before PC co-intercalation thus preventing the subsequent exfoliation of the graphite. The stability of this SEI was verified by long term cycling tests, which showed that the capacity loss of the graphite-based cell was only 1.3% after 300 cycles at 1 C. The electrolyte, 1 M LiPF₆ in PC:MTFMP (9:1 wt%), showed also a good rate capability up to 5 C on graphite. Therefore, MTFMP can be considered as a new, very promising co-solvent for PC-based electrolytes for use in lithium-ion batteries with graphite anodes.

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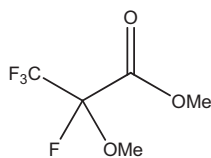
1. Introduction

Lithium-ion batteries have gained a lot of attention since their commercialization in 1990 because of their superior energy density and cycle-life compared to other battery systems. Electrolytes used in commercial lithium-ion batteries consist of mixtures of ethylene carbonate (EC) and linear carbonates, e.g., diethyl carbonate (DEC), dimethyl carbonate and ethyl methyl carbonate (EMC). So far, EC is considered as an indispensable component in the electrolyte system due to its ability to form a stable solid electrolyte interphase (SEI) on graphitic anodes. However, EC offers a poor low temperature performance [1]. To extend the liquidus range of the electrolyte, linear carbonates need to be added, which are, however, highly flammable because of their very low flash point (T_f) and high vapor pressure (e.g. DMC: $T_f = 18^\circ\text{C}$, vapor pressure = 5.8×10^3 Pa (20°C)). Therefore, their use involves safety hazards, particularly for cells with high capacity.

Propylene carbonate (PC) is a promising alternative to the state-of-the-art electrolyte solvents due to its excellent properties like low melting point (-55°C), high boiling point (240°C), and high flash point (132°C). Additionally, it enables high conductivities and good salt dissociation because of its high permittivity (64.92 at 25°C), which is close to that of EC (89.78 at 25°C) as well as its

moderate viscosity (2.53 mPa s at 25°C) [2]. Unfortunately, PC is not able to form an SEI on graphite electrodes and therefore its use leads to exfoliation of the graphite anode by solvent co-intercalation [3,4]. One possibility to circumvent this limitation consists in the use of film forming electrolyte additives, which would decompose at potentials higher than that where PC co-intercalation takes place. The decomposition must lead to the formation of a stable SEI to, therefore, protect the graphite anode from exfoliation. Different additives for PC-based electrolytes have been suggested, such as vinylene carbonate (VC) [5,6], fluoroethylene carbonate (FEC) [7], vinyl compounds [8–10], sulfite compounds [11–15], isocyanate compounds [16,17], aromatic esters [18], phenyl tris-2-methoxydiethoxy silane [19], 2-phenylimidazole [20], 2-cyanofuran [21], lithium bis(oxalato)borate (LiBOB) [22,23], N-vinyl-2-pyrrolidone [24], 1,3-propane sultone [25], and cyclic sulfates [26]. Upon addition of these additives, Li-ion cells based on graphite anodes can be cycled in PC-based electrolytes without exfoliation. However, there are just a few reports regarding the use of pure PC with additives in combination with graphite anodes. Most of the results reported, in fact, were obtained using mixtures of PC with EC and/or linear carbonates. To the best of our knowledge, only Jeong et al. reported in 2001 on the use of PC with VC as additive in combination with graphite electrodes. They showed that after 50 cycles the capacity retention was more than 96% [5]. However, these authors used LiClO₄ as lithium salt, which is not used in commercial lithium ion-batteries due to its risk of explosion in the dry form [27].

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Scheme 1. Structure of MTFMP.

In this paper, we report the results of the investigation of a new co-solvent for PC, methyl tetrafluoro-2-(methoxy) propionate (MTFMP), which is able to successfully suppress graphite exfoliation in PC-based electrolytes with LiPF_6 as lithium salt. MTFMP was first described in a patent in 2001 as a solvent for lithium-ion battery electrolytes [28]. Its structure is shown in Scheme 1. However, besides the report of the solubility of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in MTFMP no further physical or electrochemical properties of MTFMP as electrolyte component were reported. In here, we show that the use of MTFMP as co-solvent for PC enables the formation of an effective SEI on graphite electrodes, and therefore allows the use of PC in combination with such anodes. The stability of the SEI was proven by a long-term cycling test, which showed a capacity retention of 99% after 300 cycles.

2. Experimental

2.1. Electrolyte preparation

MTFMP was synthesized according to literature [29].

The conventional electrolyte 1 M LiPF_6 in EC:DEC (3:7 wt%, battery grade) and the solvent PC (purity: >99.98%) from UBE Europe GmbH and lithium hexafluorophosphate (LiPF_6 , $\geq 99.99\%$) from Sigma–Aldrich, were used as received. All work was carried out in an Argon filled glove box with water and oxygen contents below 1 ppm. Electrolyte solutions of 1 M LiPF_6 in PC:MTFMP (9:1 wt%) and 1 M LiPF_6 in PC were prepared by dissolving the appropriate amount of LiPF_6 in a premixed solution of PC:MTFMP (9:1 wt%) and in pure PC, respectively, at 25 °C. The water content of the electrolytes was determined by Karl-Fischer titration (Mitsubishi CA-200) with Aquamicon AKX (Mitsubishi) as anolyte and Aquamicon CXU (Mitsubishi) as catholyte. All electrolytes displayed a water content of lower than 10 ppm.

2.2. Electrolyte characterization

The temperature-dependent conductivity of the three electrolytes was measured in the range between -40 °C and 60 °C with a high-frequency electrochemical/materials test system (model 12608W) consisting of a Solartron 1260A impedance analyzer and a Solartron 1287A potentiostat from AMETEK GmbH. Sealed glass conductivity cells with platinized platinum electrodes from Materials Mates Italia were calibrated with a 0.01 M aqueous KCl solution. The temperature was adjusted with an environmental simulation chamber (MK 53) from Binder GmbH.

ATR-FTIR spectra were measured with a Bruker Vertex 70 and a Golden Gate ATR unit (Specac). The samples were placed on the ATR unit in the glove box. To avoid any contaminations an airtight ATR-head was used. The number of scans that were added to collect a spectrum was 120. The spectral resolution was 3 cm^{-1} .

The viscosity of the electrolytes was measured with a Rheometer (Anton Paar MCR 301) located in a dry room with a dew point lower than -76 °C. The temperature precision was $\pm 0.1\text{ K}$ and the shear rate 9000 s^{-1} .

The electrochemical stability window was determined by linear sweep voltammetry (LSV) employing a Solartron 1287A

potentiostat with a scan rate of 1 mV s^{-1} . A three-electrode setup with a platinum working electrode having a geometric surface area of $7.58 \times 10^{-3}\text{ cm}^2$, a platinum wire counter electrode, and a leakless, miniature Ag/AgCl reference electrode (Ag/AgCl 3.4 M KCl, eDAQ, model ET072), was used. The reductive electrochemical stability limit was determined by scanning from OCP towards more negative potential whereas the oxidative stability limit was obtained by scanning from OCP towards more positive potential. The stability limits were defined as the potentials at which the current density exceeded the absolute value of 0.1 mA cm^{-2} . After each measurement, the electrolyte sample was renewed and the working and counter electrodes were polished, cleaned in an ultrasonic bath, and dried for at least 2 h in a vacuum oven at 60 °C. The measurements were carried out in an argon-filled glove box.

2.3. Electrode preparation

Graphite electrodes were prepared by mixing 87% active material (Timrex T44 graphite, TIMCAL Graphite & Carbon), 5% conductive agent (Super P[®]-Li, TIMCAL Graphite & Carbon) and 8% binder (poly(vinylidene fluoride-co-hexafluoropropene), PVdF-HFP, Kynarfex[®] 2801, Arkema) with N,N-dimethylformamide (DMF, Sigma–Aldrich) with a custom-made dissolver ($\sim 10,000\text{ rpm}$) for 30 min. The obtained slurry was cast onto copper foil with a doctor blade (Olbrich) and pre-dried in a drying oven (Binder GmbH) at 60 °C for 2 h. Electrodes with a diameter of 12 mm were punched and dried overnight in a glass oven (Büchi Labortechnik AG) at 120 °C in rotary vane pump vacuum. The resulting electrodes had an active mass loading of around 2 mg cm^{-2} .

2.4. Battery tests

C-rate tests and constant current cycling experiments were performed with a battery tester Series 4000 from MACCOR, Inc. at 20 ± 2 °C using a three-electrode cell setup (Swagelok[®]). All voltage values quoted in the following refer to Li/Li⁺ potential.

The performance of the different electrolytes in combination with graphite electrodes was evaluated in cells using a graphite working electrode, an oversized $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM) cathode (serving as lithium source), as counter electrode and lithium metal as reference electrode. After three formation cycles with a charge and discharge rate of C/5 (0.10 mA cm^{-2}) in the potential range from 1.5 to 0.025 V a C-rate test was performed. The cells were always charged with a rate of 1 C (0.52 mA cm^{-2}) followed by a constant voltage step at 25 mV for 1 h. Afterwards, the cells were discharged with different rates starting from C/5 up to 5 C (2.6 mA cm^{-2}). The cycling stability of the cells was subsequently evaluated by charging with a rate of 1 C (0.52 mA cm^{-2}) plus a constant voltage step at 25 mV for 1 h and discharging with a rate of 1 C (0.52 mA cm^{-2}).

3. Results and discussion

Electrolytes with different ratios of PC and MTFMP and LiPF_6 as conductive salt were investigated regarding their SEI film-forming ability on graphite anodes. To maintain the positive properties of PC as electrolyte solvent the content of MTFMP was kept as low as possible. However, preliminary investigations showed that 10 wt% of MTFMP, which corresponds to 5.6 mol%, were necessary to achieve an effective SEI (see Fig. 1). Therefore, the physical and electrochemical measurements were carried out with the electrolyte 1 M LiPF_6 in PC:MTFMP (9:1 wt%). To fully reveal the influence of MTFMP on the physical and electrochemical properties of the electrolyte system all measurements were compared with those

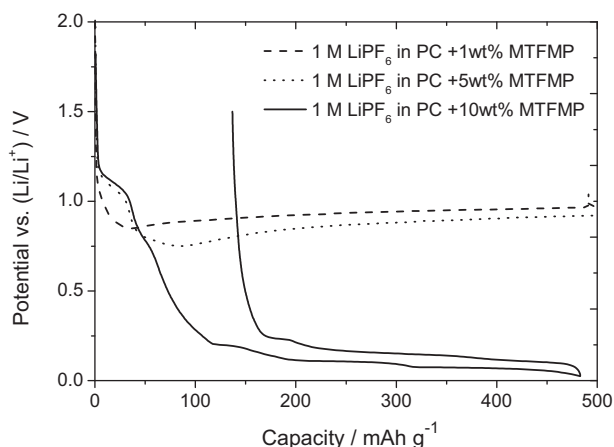


Fig. 1. Voltage profiles of the first cycle of graphite-based cells with PC electrolytes containing different amounts of MTFMP.

obtained with a PC-based electrolyte. However, battery tests using the electrolyte without MTFMP were not possible due to graphite exfoliation. To evaluate the performance of the new electrolyte with respect to a conventional electrolyte, the comparison was extended to 1 M LiPF₆ in EC:DEC (3:7 wt%) electrolyte.

3.1. Electrolyte characterization

The temperature dependent conductivity of the three electrolytes was measured in the range between -40°C and 60°C . In Fig. 2, it can be seen that the standard electrolyte 1 M LiPF₆ in EC:DEC (3:7 wt%) shows the highest conductivity up to 45°C . The two PC based electrolytes display nearly the same conductivity, with that of the pure PC-based one being slightly higher than the other. However, above 45°C and 55°C the conductivities of 1 M LiPF₆ in PC and PC:MTFMP (9:1 wt%), respectively, are higher than that of 1 M LiPF₆ in EC:DEC (3:7 wt%).

The conductivity of electrolytes depends on two main factors: the amount of free charge carriers (ions) in the electrolyte and the ability of these charge carriers to move in the electric field, which is limited by the viscosity of the electrolyte solution. It is known that ionic dissociation, and thus the number of free charge carriers, increases with increasing relative permittivity ϵ of the used solvents [30]. To investigate the ionic dissociation in the different electrolytes ATR-FTIR-spectra were recorded with focus on the signals at 741 cm^{-1} and 867 cm^{-1} . These signals have been assigned to Li⁺...PF₆⁻ ion pairs, which are formed in solvents with low relative

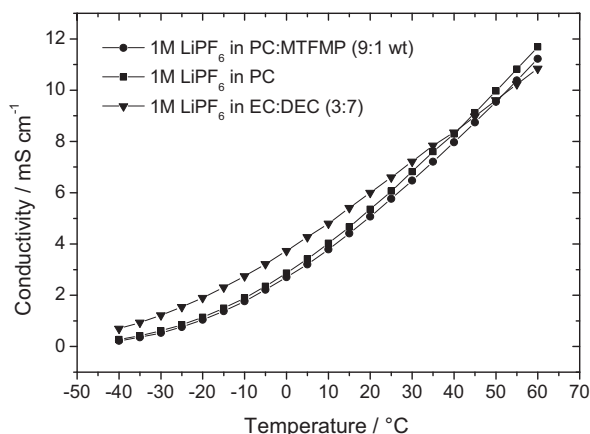


Fig. 2. Temperature dependent ionic conductivity of the electrolytes.

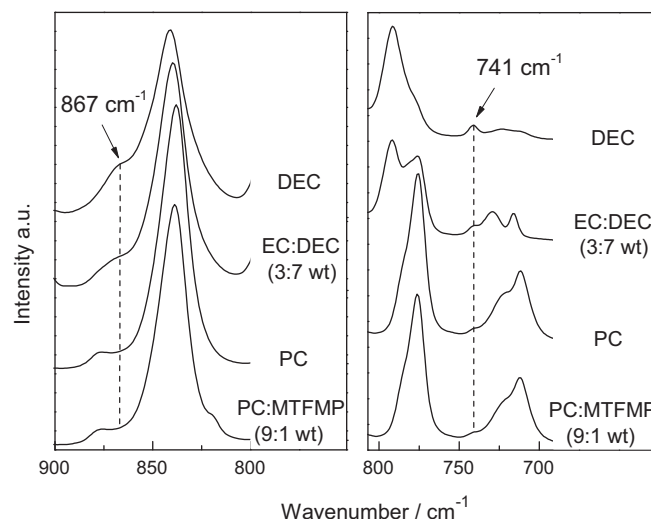


Fig. 3. ATR-IR spectra of 1 M LiPF₆ in solvents with different relative permittivities.

permittivity where the salts might be dissolved but not fully dissociated [31]. In Fig. 3 the spectra of the three investigated electrolytes are given. For comparison, the spectrum of 1 M LiPF₆ in DEC is also shown, as DEC is an example for a good solvent with low relative permittivity (2.81 at 25°C). In fact, LiPF₆ is well dissolved in DEC, however, it can be seen in Fig. 3 that both characteristic peaks for Li⁺...PF₆⁻ ion pairs are present in the spectrum. The addition of the high relative permittivity solvent EC ($\epsilon = 89.78$ at 25°C) to DEC results in a reduced intensity of both peaks, which indicates an increased amount of dissociated ions. Nevertheless, some ion pairing is visible as the content of the high relative permittivity solvent is limited to 30 wt% to avoid depressing the low temperature conductivity.

In contrast, for both PC based electrolytes, the intensity of the peak at 741 cm^{-1} is strongly reduced while the peak at 867 cm^{-1} is completely vanished. These electrolytes contain predominantly free ions rather than ion pairs, due to the high relative permittivity (64.92 at 25°C) of PC, which enables the dissociation of the salt.

Based on the results obtained by this method one should expect the conductivity of the two PC containing electrolytes being the same and the conductivity of the EC:DEC based electrolyte being lower than the former ones. However, it is known from the Walden rule that the conductivity is also dependent on the viscosity. Therefore, this would just be true if the viscosities of all three electrolytes were the same. In Table 1 the viscosities of the three electrolytes at 20°C and 40°C are given. It can be seen that at 20°C the viscosities of the PC based electrolytes are significantly higher than that of the EC:DEC based electrolyte. With increasing temperature, however, this difference becomes smaller.

Comparing the results of the viscosity, conductivity and ATR-FTIR measurements it appears as, at 20°C , the viscosity has the highest impact on the conductivity. In agreement with the viscosity values, 1 M LiPF₆ in EC:DEC (3:7 wt%) displays the highest conductivity (6.0 mS cm^{-1}) followed by 1 M LiPF₆ in PC (5.4 mS cm^{-1}) and 1 M LiPF₆ in PC:MTFMP (9:1 wt%) (5.1 mS cm^{-1}). However, with increasing temperature the influence of the degree of ionic

Table 1
Viscosities of 1 M LiPF₆ in different solvents at different temperatures.

Temperature/ $^{\circ}\text{C}$	Viscosity $\eta/\text{mPa s}$		
	PC:MTFMP (9:1 wt%)	PC	EC:DEC (3:7 wt%)
20	7.8	7.6	4.8
40	5.0	5.0	3.3

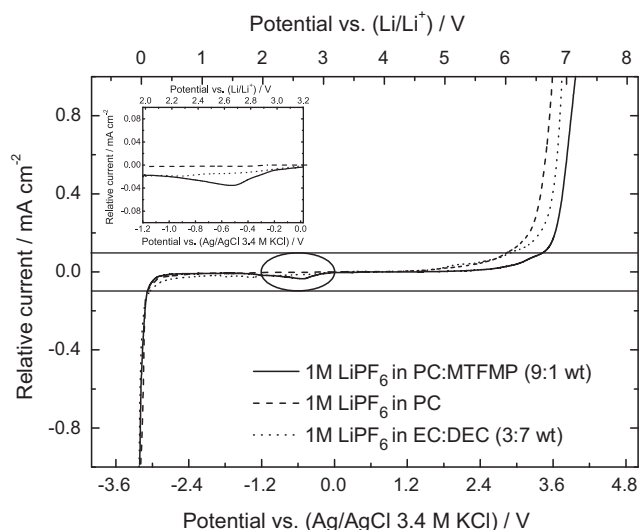


Fig. 4. Electrochemical stability window of three different electrolytes on Pt. Scan rate: 1 mV s^{-1} .

dissociation seems to become dominant, as the conductivity does not scale linearly with temperature although the viscosity does.

The electrochemical stability window of the three different LiPF_6 based electrolytes was measured by scanning the potential of a Pt working electrode immersed in the different electrolytes (1 mV s^{-1}). The absolute current limit of 0.1 mA cm^{-2} was selected as onset of decomposition reactions. The results of these measurements are shown in Fig. 4.

During the positive potential sweep the new electrolyte, 1 M LiPF_6 in PC:MTFMP (9:1 wt%), displays the highest stability among the three investigated. The potential at which the limiting current density of 0.1 mA cm^{-2} was reached was 0.5 V higher than that for the standard electrolyte (1 M LiPF_6 in EC:DEC (3:7 wt%)). If the two PC-based electrolytes are compared, the oxidative stability of the electrolyte containing 10 wt% MTFMP is even 0.6 V higher than that of the electrolyte based on PC only. These results indicate that the co-solvent MTFMP stabilizes the PC based electrolyte against oxidation at the platinum electrode. This is surprising since the oxidative stability of ethers is normally limited to approximately 4 V vs. Li/Li^+ [32]. However, the stability of the ether function of MTFMP seems to be increased due to the high degree of fluorination. The CF_3 group as well as the fluorine atom are strong electron-withdrawing substituents, which reduce the electron density and thus stabilize the ether group of MTFMP towards oxidation. The same applies to the ester group of MTFMP.

During the negative potential sweep all three electrolytes are electrochemically stable down to $0.1 \text{ V vs. Li/Li}^+$. However, the reductive limit on platinum electrodes is not representative for the reductive stability of the electrolyte. At such a low potential, different reactions, like lithium plating and Li–Pt alloy formation, can occur that also cause increase in current density. Consequently, it is not possible to clearly assign the current density increase to the decomposition of the electrolyte. Additionally, the reactivity of the electrolyte at the model electrode Pt is different from the reactivity towards real electrode materials [33]. However, one important feature that can be seen from the negative potential sweep is that the MTFMP-containing electrolyte showed an irreversible faradaic reaction in the range between 3.2 V and $2.0 \text{ V vs. Li/Li}^+$, whereas the other two electrolytes did not show any increase in current density until $0.1 \text{ V vs. Li/Li}^+$ (see insert in Fig. 4). The observed faradaic reaction is due to MTFMP decomposition, which might be the reaction for the SEI formation on the graphite electrode surface before PC co-intercalation and thus exfoliation of the graphene layers, occur.

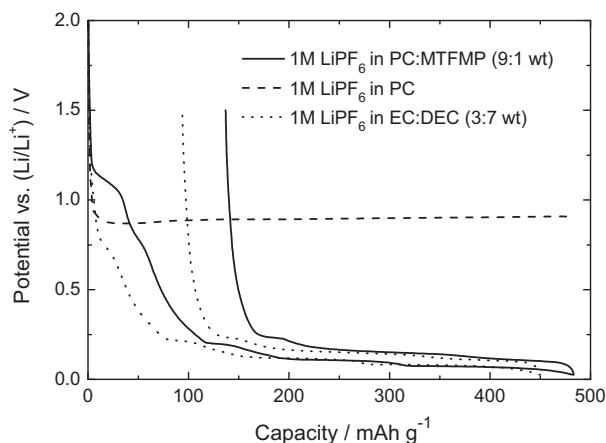


Fig. 5. Voltage profiles of the first cycle of graphite-based cells with different electrolytes.

3.2. Battery tests

To verify the effect of MTFMP in PC-based electrolytes in terms of formation of an effective SEI, cells with a graphite working electrode were cycled in PC-based electrolytes with and without MTFMP. For comparison, the same test was also performed with the standard electrolyte 1 M LiPF_6 in EC:DEC (3:7 wt%). To avoid limitation of cyclability due to dendritic growth, oversized NCM cathodes were used as lithium source instead of lithium metal foil.

In Fig. 5, the first cycle of the cells with the different electrolytes, is shown. The standard electrolyte shows just a small plateau at around $0.8 \text{ V vs. Li/Li}^+$, which is known to be associated with the formation of an SEI via the decomposition of EC. The formation of the SEI enables cycling of the graphite anode without exfoliation. In contrast, when the PC based electrolyte is used a continuous electrochemical reaction at $0.9 \text{ V vs. Li/Li}^+$ takes place, which is associated to the intercalation of PC-solvated lithium ions leading to graphite exfoliation [34]. Due to the exfoliation, the graphite particles are destroyed and, consequently, cycling of the cell is not possible. If 10 wt% MTFMP is added to the PC-based electrolyte, however, the first faradaic reaction occurs already at $1.2 \text{ V vs. Li/Li}^+$. This reaction is associated with the decomposition of MTFMP, which could already be observed during the ESW measurements. The difference in the potential region for the decomposition of MTFMP between the ESW measurements (between 3.2 V and $2.0 \text{ V vs. Li/Li}^+$) and the first cycle voltage profiles (between 1.2 V and $0.8 \text{ V vs. Li/Li}^+$) can be explained by the different working electrodes used for the experiments. For the ESW measurements Pt was used as working electrode whereas for the first cycle voltage profiles graphite served as working electrode. When the potential is further decreased, some decomposition of PC is observed. However, this does not seem to have an influence on the cyclability of the cells.

These results show that MTFMP is able to form an effective SEI preventing the intercalation of the solvated lithium ions and thus, exfoliation of the graphite particles. Additionally, the cell with 1 M LiPF_6 in PC:MTFMP (9:1 wt%) displays a high coulombic efficiency of 72% in the first cycle, which is 7% lower than that of the cell containing the standard electrolyte (79%). It is difficult to compare these efficiencies with those reported in literature as the irreversible specific charge during the first cycle strongly depends on the crystallinity and the morphology of the investigated graphitic material [35] and is therefore different for different graphitic materials. The efficiency of the 2nd and 3rd cycle is 93% and 95% for the PC:MTFMP mixture and 97% and 99% for the EC:DEC mixture.

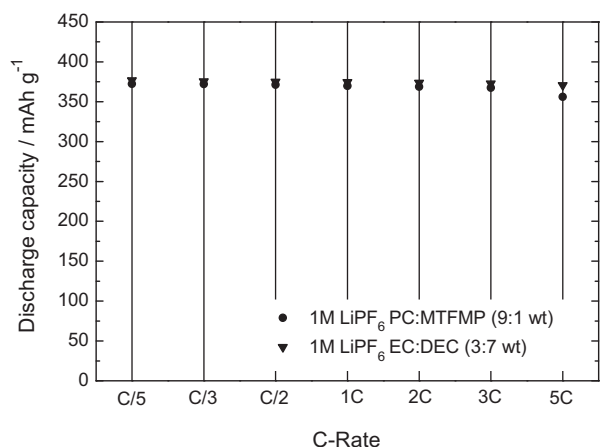


Fig. 6. Rate performance of graphite-based cells with different electrolytes at RT in the potential range from 1.5 V to 0.025 V.

The high rate capability of 1 M LiPF₆ PC:MTFMP (9:1 wt%) and 1 M LiPF₆ in EC:DEC (3:7 wt%) was determined by a C-rate test with constant charge rates and different discharge rates from C/5 up to 5 C. As the pure PC-containing electrolyte causes exfoliation it was not possible to further investigate this electrolyte in cells. The results of the C-rate test are shown in Fig. 6. Up to a C-rate of 3 C both cells display a similar discharge capacity with the one containing 1 M LiPF₆ in PC:MTFMP (9:1 wt%) being just 5 mAh g⁻¹ lower than that comprising the conventional electrolyte. This difference is within the error range of the measurement originating from the electrode weight estimation and alignment. It is only at a discharge rate of 5 C that the capacity of the cell with 1 M LiPF₆ in PC:MTFMP (9:1 wt%) decreased more substantially than that with the electrolyte 1 M LiPF₆ in EC:DEC (3:7 wt%). However, the cell still reached a capacity of 356 mAh g⁻¹, which was only 15 mAh g⁻¹ lower than that of the cell comprising the standard electrolyte.

To verify the long-term stability of the SEI formed during the first few cycles by MTFMP decomposition, the cycling performance of 1 M LiPF₆ in PC:MTFMP (9:1 wt%) containing cells was investigated. As shown in Fig. 7, the cells showed very good capacity retention of 99% after 300 cycles at a fairly high C-rate of 1 C. Therefore, it can be concluded that the presence of MTFMP in PC-based electrolytes leads to the formation of a stable and effective SEI, which is able to protect graphite anodes against exfoliation.

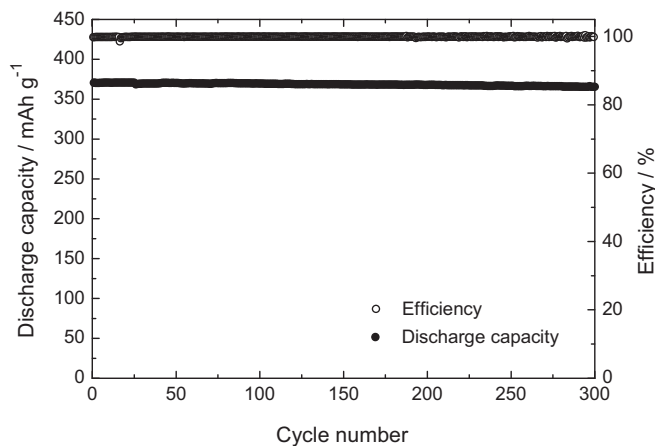


Fig. 7. Cycling performance of a graphite electrode in 1 M LiPF₆ in PC:MTFMP (9:1 wt%) electrolyte at RT. The cells were charged at C rate plus 1 h of constant voltage (25 mV) and discharged at C rate in the potential range from 1.5 to 0.025 V.

4. Conclusions

In this paper a new SEI-film forming co-solvent for lithium-ion battery electrolytes based on PC was explored. The results showed that the addition of 10 wt% of this co-solvent fully prevents exfoliation thus enabling the use of PC-based electrolytes in combination with graphite electrodes. The formation of an effective SEI is observed during the initial 3 cycles. Long-term cycling tests proved the stability of this SEI layer as the capacity retention was 99% after 300 cycles. In addition, the rate capability of this new electrolyte showed extremely promising results. Further evaluations indicated that MTFMP hardly affects the conductivity and even increases the oxidative electrochemical stability of the electrolyte. These results support the feasibility of using MTFMP as co-solvent for PC in graphite based lithium-ion batteries.

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