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Design and electrochemical properties of novel fluorinated electrolytes for lithium metal batteries

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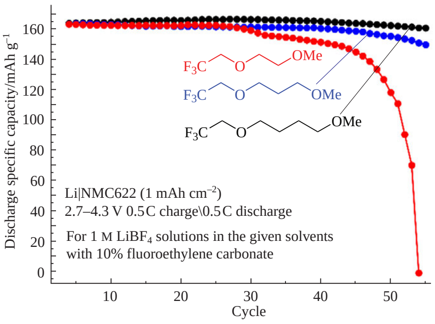
Synthesis and electrochemical study of novel trifluorinated diethers, namely, α-methoxy-ω-(2,2,2-trifluoroethoxy)-alkanes, as potential candidates for new-generation electrolyte solvents for lithium-metal batteries are presented. The trifluoro diethers were tested in cell configurations implying cathodes with high nickel content and revealed Coulombic efficiencies exceeding 99.9% and specific discharge capacity retention up to 99% over 55 cycles for potentials up to 4.5 V. This study opens up new prospects in targeted design of organic ether molecules as lithium-metal batteries electrolyte components.



Keywords: electrolytes, lithium-ion batteries, lithium-metal batteries, ethers, organofluorine compounds, nickel-rich cathodes.

Over the past three decades, lithium-ion batteries (LIBs) have totally dominated the niche of portable electronic devices and now continue to shape the outfit of electric vehicles and define the capabilities of stationary energy storage systems thus becoming an indispensable part of modern economy and lifestyle.[1] Their rapid market proliferation would have not been possible without continuous improvements in the LIB technology mostly regarding the values of specific energies.[2–4] Further substantial advancements of energy density parameters are expected by introducing a Li-metal anode instead of traditional graphite-based ones, which results in a so-called lithium-metal battery (LMB). Unfortunately, the progress in LMBs is limited by the low thermodynamic stability of conventional carbonate-based electrolytes on metallic Li. Numerous uncontrollable side processes between Li metal and electrolyte result in the formation of a solid electrolyte interphase (SEI). Fragile SEI layers easily undergo mechanical failure during battery operation causing not only constant consumption of both electrolyte and lithium but also lithium-dendrite growth, which leads to low Coulombic efficiency and poor cycle life of LMBs.[5–7] Therefore, careful selection of electrolytes with proper reactivity, electrochemical stability, ion transport, and solvation ability is necessary to stabilize the SEI layer and extend the cycle life.[8,9]

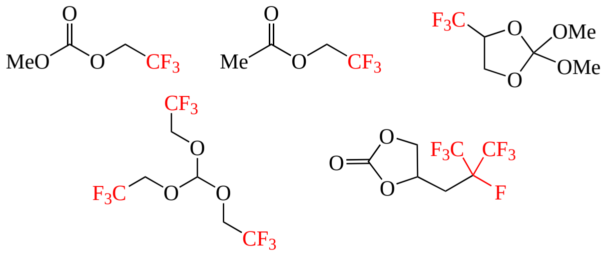
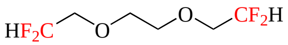


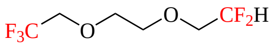
Figure 1 Fluorine-containing electrolytes.

The carbon–fluorine bond is known to be one of the strongest single carbon–heteroatom bonds, which makes organofluorine solvents less reactive. Due to the robustness of organofluorine compounds, the resulting electrolytes are nonflammable and electrochemically stable. Fluorinated organic carbonates, esters and ortho esters shown in Figure 1 and many others are proven to create a reliable LiF-rich SEI,[10–12] which is crucial for the safe operation of LMBs.[13–17]

The inactivity of fluorinated ethers towards metallic Li due to the absence of highly reactive functional groups makes them promising electrolyte components for commercial utilization.[18] Strong electron-withdrawing properties of fluorine atom extend the oxidative stability of fluorinated ethers in comparison to their fluorine-free counterparts.[19–21] The effect of the introduction of –CF_2– and CF_3-moieties into the structure of 1,2-diethoxyethane solvent on the electrochemical properties of the electrolyte was shown, and its fluorinated analogues 1,2-bis(2,2-difluoroethoxy)ethane **A** and 2-[2-(2,2-difluoroethoxy)ethoxy]-1,1,1-trifluoroethane **B** were proven to contribute to the high Coulombic efficiency and high-voltage stability of Li||NMC811cells with 1.2 M lithium bis(fluorosulfonyl)imide $LiN(SO_2F)_2$ as an electrolyte salt.[22]



A



B

Coordination environment of transferring cation plays an important role in the performance of electrolyte.[23,24] 1,2-Dimethoxyethane and 1,3-dimethoxypropane are known to form a five- and six-membered chelate ring configuration with two oxygen atoms and one fluorine atom coordinating Li^+ ions,

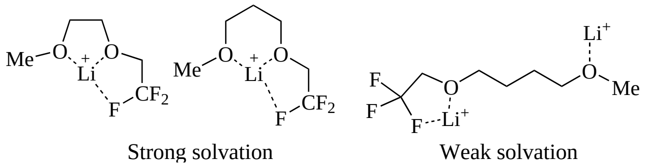


Figure 2 Possible solvation of Li$^+$ with O and F atoms.

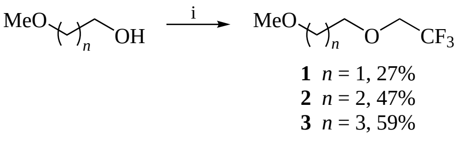
leading to strong Li$^+$-solvation, however the chelating effect disappears when the number of –CH$_2$– units reaches four (Figure 2).[25] Our idea behind this study was to analyze how well alkoxy and trifluoromethoxy groups coordinate Li$^+$ ions and, as a result, affect the electrochemical properties of electrolytes.

Herein, we report the synthesis and electrochemical properties of a series of α-(methoxy)-ω-(2,2,2-trifluoroethoxy)alkanes **1**–**3**, where 1-methoxy-3-(2,2,2-trifluoroethoxy)propane **2** and 1-methoxy-4-(2,2,2-trifluoroethoxy)butane **3** are new compounds (Scheme 1). These compounds differed noticeably from the abovementioned structures **A** and **B**.[22] We were planning to establish relationships between the chemical structures of **1**–**3** and the performance of the electrolyte based on them in Li-metal anode cells. Next-generation high-energy cathode materials $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622) and $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811) were chosen for this study because of their ability to provide high specific capacities and voltages.[26,27]

We prepared three fluorinated dialkoxyalkanes with different spatial distances between 2,2,2-trifluoroethoxy and methoxy groups. For the synthesis of 1-methoxy-2-(2,2,2-trifluoroethoxy)-ethane **1** and its homologues **2**, **3**, we elaborated a general procedure (see Scheme 1). At first, deprotonation of ω-methoxyalkanol with sodium hydride was carried out, and then the resulting alcoholate was treated with 2,2,2-trifluoroethyl tosylate to give the desired α-methoxy-ω-(2,2,2-trifluoroethoxy)-alkane in moderate-to-high yields (47–80%). As long as the isolation of individual **1**–**3** was performed *via* distillation under reduced pressure, we supposed that the boiling points of all three compounds were high enough to be used as electrolyte components, which were measured and validated later on (Table 1).

Earlier,[28] an electrolyte based on **1**/ethylene carbonate (1 : 1 v/v) mixture with 1 M LiPF$_6$ was investigated in LiCoO$_2$||Li cells and was found to have better cycling efficiency and Coulombic efficiency in comparison to the same cell configuration with non-fluorinated 1-ethoxy-2-methoxyethane. Considering that, we intended to test an electrolyte with trifluoro diether **1** as the main component in NMC622||Li and NMC811||Li cells.

To make sure that the synthesized compounds **1**–**3** were suitable for the use as electrolyte solvents, we measured their viscosities (see Table 1). The viscosity values for them lied in the range of 0.980–1.376 mPa s, which was low enough to meet common standards. Since the most widely used LiPF$_6$ or LiN(SO$_2$F)$_2$ salts were found to react with α-methoxy-ω-(2,2,2-trifluoroethoxy)alkanes or undergo decomposition in standard stainless steel coin cells, LiBF$_4$ was chosen as a salt. Fluoroethylene carbonate (FEC) was added to create a robust SEI. The solutions of 1 M LiBF$_4$ in the mixture of trifluoro diethers **1**–**3** and FEC (9 : 1 v/v) were proven to have appropriate viscosities (see Table 1). The electrolytes of such a composition were applied in all further experiments.



1 *n* = 1, 27%
2 *n* = 2, 47%
3 *n* = 3, 59%

Scheme 1 *Reagents and conditions*: i, NaH, THF, then CF$_3$CH$_2$OTs, Δ.

Table 1 Properties of synthetized α-methoxy-ω-(2,2,2-trifluoroethoxy)-alkanes **1**–**3**.

Compound	bp/°C	Viscosity/mPa s	
		neat	with 1 M LiBF$_4$ and 10 vol% FEC
1	108	1.376 ± 0.052	4.048 ± 0.092
2	122	0.988 ± 0.039	3.712 ± 0.237
3	158	0.980 ± 0.083	2.612 ± 0.139

In order to evaluate the anodic stability of compounds **1**–**3**, we used linear sweep voltammetry in Li||stainless steel coin-cells. As we can see (Figure S10 in Online Supplementary Materials), trifluoro diether **1** is more vulnerable to high voltage than its higher homologues **2** and **3**. Nevertheless, all three electrolytes are stable at voltages below 5.5 V and more stable than the commercial 1 M LiPF$_6$ in ethylene/dimethyl carbonates (EC/DMC, 1 : 1 v/v).

Electrochemical stability towards Li was evaluated using Li||Li symmetric cells. A current density of 0.5 mA cm^{-2} and an areal capacity of 0.5 mAh cm^{-2} were applied for Li plating and stripping. As shown in Figure S11, after 100 h of cycling the overpotential of the 1 M LiBF$_4$/**1**/FEC (9 : 1 v/v) shows the highest growth and reaches 1.5 V within 100 h period due to electrochemical instability and resistance building up. This system demonstrated significantly lower overpotential growth with less than 0.3 V within the same period while electrolyte with homologue **2** was the most stable and comparable to commercial 1 M LiPF$_6$/EC/DMC (1 : 1 v/v), for which overpotential growth did not exceed 0.1 V.

The change of Coulombic efficiency (CE) over cycling represents anodic stability of electrolytes 1 M LiBF$_4$ in **1**–**3** with FEC in Li||NMC622 and Li||NMC811 cells at 4.3 V with cycling rate 0.5 C. Therefore, in case of electrolytes based on **2**, **3** in Li||NMC622 cells, three to four activation cycles were needed before ramping up to 99.85 and 99.70% CE, respectively, which is comparable to the commercial 1 M LiPF$_6$ EC/DMC, but for the case with **1** CE only reached 98.80% maximum [Figure 3(*a*)]. It indicates a more pronounced tendency of oxidation for compound **1** and generous amounts of side processes occurring in coin-cells. Specific discharge capacity was recorded in Li||NMC622 and Li||NMC811 cells within the 2.7–4.3 V range at

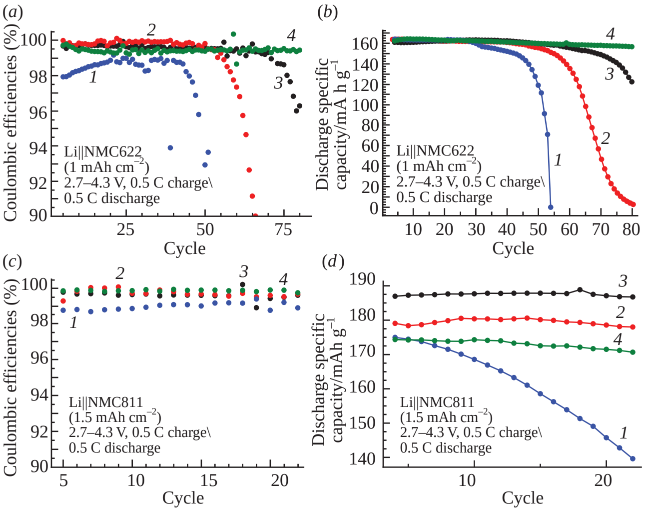


Figure 3 (*a*, *c*) Coulombic efficiencies and (*b*, *d*) cycling performances of (*a*, *b*) Li||NMC622 and (*c*, *d*) Li||NMC811 for 1 M LiBF$_4$ solutions in trifluoro diethers **1** (curves *1*), **2** (curves *2*) and **3** (curves *3*) with 10% fluoroethylene carbonate. For comparison: curves *4* relate to 1 M LiPF$_6$ solution in ethylene/dimethyl carbonates (1:1).

0.5 C charge/discharge rate for all three studied electrolytes and 1 M LiPF$_6$ in EC/DMC as the reference. In terms of cycling performance, the electrolyte based on **1** in the Li||NMC622 cell configuration showed decent proficiency up to 42 cycles (capacity loss 9%), then followed with 15% capacity loss over next 40 cycles and severe decomposition after 48 cycles. Electrolytes based on 1 M LiBF$_4$ in **2**, **3** with FEC were proven to be more effective in the same cell configuration with 90 and 99% capacity retention over 55 cycles, respectively, however both did not exceed commercial electrolyte [Figure 3(*b*)]. As it shown in Figure S12, the poorly performing 1 M LiBF$_4$ in **1**/FEC (9 : 1 v/v) electrolyte demonstrated a drastic polarization increase during cycling while other two electrolytes **2**, **3** showed slowly evolving polarization accompanied by progressive capacity loss. Such behaviour for compounds **2**, **3** may be explained by the higher solvation energy for the six-membered **2**-Li$^+$ complex which is reflected by slightly higher CE and lower cycling performance of the corresponding electrolyte. However, diether **3** bonded with two Li$^+$ cations undergoes a desolvation step easier, which makes it a more potent electrolyte in terms of charge-transportation and, as a result, cycling efficiency.

To investigate the performance of 1 M LiBF$_4$ in **1**–**3**/FEC electrolytes with higher nickel-content cathodes, we assembled and tested a series of cells with the Li||NMC811 configuration. Coulombic efficiency for the electrolyte based on **1** was found to be noticeably higher than that in the Li||NMC622 cells and reached 99.00% after six cycles, however it was still lower than CE of commercial 1 M LiPF$_6$ EC/DMC electrolyte [Figure 3(*c*)]. In cases of compounds **2**, **3**, CE drops after 8 cycles from 99.95 to 99.50% and from 99.75 to 99.55%, respectively, which indicates significant electrolyte consumption due to the side reactions. In terms of cycling efficiency, 1 M LiBF$_4$ in **1**/FEC was proven to be the most unstable with 20% capacity loss in 22 cycles. Other two electrolytes **2** and **3** demonstrated higher initial specific capacities (181 mAh g^{-1} for **2**, 187 mAh g^{-1} for **3**) and decent performance over 25 cycles with capacity retentions over 98 and 99% for **2** and **3**, respectively [see Figure 3(*d*)]. Polarization growth during cycling for all the three studied electrolytes **1**–**3** is much more prominent than in case of Li||NMC811 cell configuration and its value reaches 0.4 V in just 24 cycles (Figure S13).

For the best performing electrolyte, 1 M LiBF$_4$ in **3**/FEC, cycling tests in a wider potential window were carried out. Specific capacity for the Li||NMC622 cells within the potential range of 2.7–4.5 V was predictably higher than for the 2.7–4.3 and 2.7–4.4 V ranges (184, 176 and 165 mAh g^{-1}, respectively) while also maintaining good stability and CE (99.75–99.85%) during 50 cycles [Figure 4(*b*)]. Unfortunately, compound **3** was found to be less effective at 4.5 V with a CE drop from 99.35 to 99.00% after only10 cycles [Figure 4(*a*)].

Next, we examined the behaviour of 1 M LiBF$_4$ in **3**/FEC in the Li||NMC811 cell configuration at higher potentials. Coulombic efficiencies for cycling up to 4.5 V were found to be insufficient (average 98.10%) and gradually declined over cycling [see Figure 4(*c*)]. The same tendency was observed for the specific capacity at 4.5 and 4.4 V, where capacity loss amounted to 12 and 5%, respectively, in 23 cycles [see Figure 4(*d*)]. Therefore, we concluded that the electrolyte based on **3** might promote NMC811 degradation at high potentials due to its lower stability.[26]

In conclusion, α-methoxy-ω-(2,2,2-triluoroethoxy)alkanes **1**–**3** were proven to be prospective as electrolyte solvents in combination with fluoroethylene carbonate (9 : 1 v/v) and 1 M LiBF$_4$ as an electrolyte salt in cells with nickel-rich cathodes. Systems 1 M LiBF$_4$ in **2**/FEC and **3**/FEC (9 : 1) demonstrated high cycling and Coulombic efficiency (>90% capacity retention over 55 cycles and >99.7% CE) in Li||NMC622. Compound **1** was shown to maintain its stability during 28 cycles (>90% capacity retention), however the fact that CE never reached 99% indicated its insufficient electrochemical stability. Overall CE values were found to be higher in case of Li||NMC811 cell setup (99.00–99.95%), but cycling stability for compound **1** turned out to be very low (20% specific capacity loss over 23 cycles). The best-performing electrolyte 1 M LiBF$_4$ **3**/FEC (9 : 1 v/v) was discovered to be proficient at voltages up to 4.5 V (>90% capacity retention over 80 cycles) in Li||NMC622 cells, however it degraded quickly when combined with NMC811.

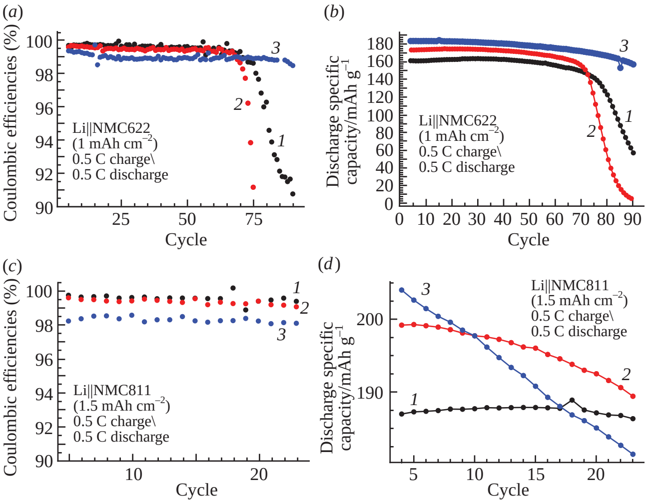


Figure 4 (*a*, *c*) Coulombic efficiencies and (*b*, *d*) cycling performances of (*a*, *b*) Li||NMC622 and (*c*, *d*) Li||NMC811 with 1 M LiBF$_4$ solutions in trifluoro diether **3** with 10% fluoroethylene carbonate for voltages from 2.7 to 4.3 V (curves *1*), to 4.4 V (curves *2*) and to 4.5 V (curves *3*).

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2024.04.033.

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