Single-ion conducting polymer electrolyte for Li||LiNi$_{0.6}$Mn$_{0.2}$Co$_{0.2}$O$_2$ batteries—impact of the anodic cutoff voltage and ambient temperature

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Abstract

Polymer-based electrolytes potentially enable enhanced safety and increased energy density of lithium-metal batteries employing high capacity, transition metal oxide–positive electrodes. Herein, we report the investigation of lithium-metal battery cells comprising Li[Ni$_{0.6}$Mn$_{0.2}$Co$_{0.2}$]O$_2$ as active material for the positive electrode and a poly(arylene ether sulfone)-based single-ion conductor as the electrolyte incorporating ethylene carbonate (EC) as selectively coordinating molecular transporter. The resulting lithium-metal battery cells provide very stable cycling for more than 300 cycles accompanied by excellent average Coulombic efficiency (99.95%) at an anodic cutoff potential of 4.2 V. To further increase the achievable energy density, the stepwise increase to 4.3 V and 4.4 V is herein investigated, highlighting that the polymer electrolyte offers comparable cycling stability, at least, as common liquid organic electrolytes. Moreover, the impact of temperature and the EC content on the rate capability is evaluated, showing that the cells with a higher EC content offer a capacity retention at 2C rate equal to 61% of the capacity recorded at 0.05 C at 60 °C.

We dedicate this manuscript to Professor Roberto Marassi, whose dedication to science has been a great example for many scientists.

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Introduction

Rechargeable lithium-metal batteries are considered the next great leap forward toward higher energy densities [1]. Nevertheless, the severe risk of lithium dendrite formation, potentially causing a short circuit of the cell, and the continuous electrolyte decomposition at the electrode|electrolyte interface have so far hampered the commercial exploitation of such batteries—with one little exception: lithium-polymer batteries comprising an electrolyte based on poly(ethylene oxide) (PEO) [2]. This polymer electrolyte, however, suffers of two major drawbacks related to the operating temperature of about 60–80 °C (especially during charge, when Li plating occurs) and the choice of the active material for the positive electrode, which is limited to materials that are de-/lithiated below 4 V, such as LiFePO$_4$ [2–6]. These two issues originate from the facts that the charge transport is coupled with the segmental motion of the polymer, which is faster the higher the temperature, and that the lithium-coordinating ether group and/or terminal hydroxyl groups are not sufficiently stable toward

oxidation beyond 4 V [4, 7–11]. Another issue is the potential reversed cell polarization at elevated current densities, leading to accelerated cell failure and favoring inhomogeneous (dendritic) lithium deposition [12–15].

Very recently, we have reported a new multi-block co-poly(arylene ether sulfone) electrolyte, which addresses these issues by covalently tethering the anionic function to the polymer backbone, stabilizing the ether group through adjacent electron-withdrawing groups, and introducing, e.g., ethylene carbonate (EC) as "molecular transporter" to actively facilitate Li^+ conduction rather than simply plasticizing the ionomer, the latter effect being facilitated by the selective coordination of EC to the ionophilic block (psi-PES) in which the charge transport occurs, while the ionophobic blocks (FPES) provide mechanical stability [16]. This nanophase-separated, single-ion–conducting, multi-block copolymer electrolyte comprising EC allows for the stable cycling of Li||Li[Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$]O$_2$ (NMC$_{111}$) full cells with an anodic cutoff voltage of 4.2 V for more than 200 cycles at 40 °C with a specific capacity of about 100 mAh g^{-1} at 0.2 C (32 mA g^{-1}) [16].

Herein, we investigate the use of this multi-block copolymer electrolyte in high-energy Li||Li[Ni$_{0.6}$Mn$_{0.2}$Co$_{0.2}$]O$_2$ (NMC$_{622}$) cells, as schematized in Fig. 1, with particular regard to the impact of the stepwise increasing anodic cutoff voltage from 4.2 V to 4.3 V and 4.4 V. Moreover, we investigated the effect of increasing the EC concentration and the ambient temperature on the achievable rate capability, revealing a very good capacity retention even at 2 C thanks to an ionic conductivity well above 1 mS cm^{-1} under such conditions.

Experimental

Copolymer synthesis

The synthesis of the partially fluorinated multi-block poly(arylene ether sulfone) with covalently tethered lithium perfluorosulfonimide functions (herein referred to as SI), serving as electrolyte, and its characterization have been described in detail in Nguyen et al. [16]. Briefly, the block copolymer backbone (with block lengths of 15 kg mol^{-1}) was synthesized via co-polycondensation and subsequently region-selectively brominated in order to allow for the covalent tethering of the sulfonimide anion using Ullman's coupling reaction [17] and lithium 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoro-2-iodoethoxy)ethanesulfonimide (I-psiLi) as precursor. EC was purchased from Merck or BASF and used as received. The copolymer was characterized via ^{1}H NMR and ^{19}F NMR spectroscopy to confirm the molecular architecture. Size-exclusion chromatography coupled with a multiangle light scattering detector revealed a weight-average molecular weight (M$_w$) of 724 kg mol^{-1}. The solvent content (SC), indicated as x in SIx%, is defined as the ratio between the mass of the EC-swollen membrane (M$_s$) minus the mass of the dry membrane (M$_d$) and M$_s$, multiplied by 100% [16]:

$$SC = \frac{Ms - Md}{Ms} \times 100\%$$

The handling and processing of the ionomer membranes were conducted either in an argon-filled glove box or in the dry room to avoid a relevant impact of moisture.

Fig. 1 Molecular architecture of the multi-block copolymer electrolyte and schematic illustration of its nanophase separation including the EC molecules selectively coordinating the ionophilic blocks as well as the eventual Li||NMC$_{622}$ full cell incorporating such electrolyte
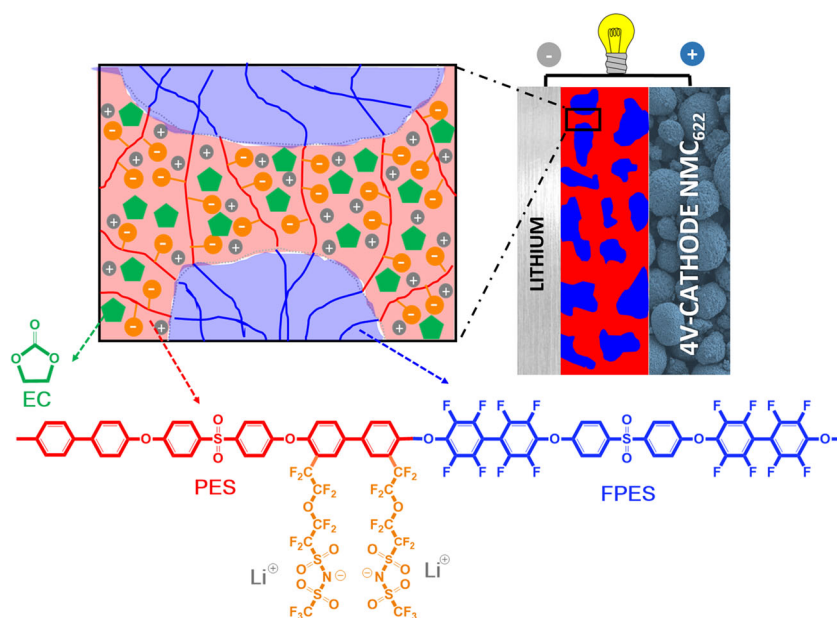
Electrode preparation and electrochemical characterization

The NMC_{622} electrode preparation was performed in the dry room as well. NMC_{622} (industrial source) was dispersed together with Super C65 (IMERYS) and poly(vinylidene difluoride) (PVdF, Solvay) in N-methyl-2-pyrrolidone (NMP, Aldrich) via magnetic stirring (3 h at 500 rpm). The resulting slurry was cast on aluminum foil using a laboratory-scale doctor blade with a wet film thickness of 130 μm. The resulting electrode sheets were dried at 60 °C overnight. Disk-shaped electrodes (∅ = 12 mm) were punched from the thus pre-dried electrode sheets and subsequently dried at 120 °C for 12 h under vacuum. Eventually, the electrodes were pressed at 10 t for 10 s. The total electrode composition was 88 wt% NMC_{622}, 7 wt% Super C65, and 5 wt% PVdF. The active material mass loading (i.e., the mass loading of NMC_{622}) was around 2.0 ± 0.2 mg cm^{-2}. For the electrochemical characterization, two-electrode, Swagelok-type cells were assembled sandwiching the ionomer electrolyte membrane between the NMC_{622} electrode and the lithium metal electrode (Honjo, battery grade). The whole cell was subjected to a pressure (4-5 t) for 3 min to infiltrate the ionomer electrolyte into the porous NMC_{622} electrode. Galvanostatic cycling was conducted using a Maccor 4000 battery tester. The temperature was controlled by placing the cells in climatic chambers (Binder). The cathodic cutoff voltage was kept constant at 2.8 V throughout all the tests reported herein, while the anodic cutoff voltage was varied from 4.2 to 4.3 V and 4.4 V. A dis-/charge rate of 1C corresponds to a specific current of 160 mA g^{-1}, with the mass in g referring to the active material
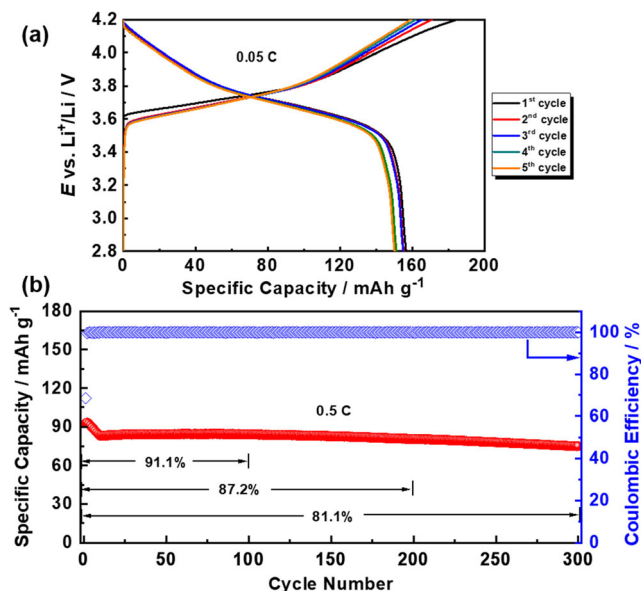
mass loading, i.e., NMC_{622}. Accordingly, all capacity values reported herein refer to the active material mass loading as well. We have chosen this specific current to define a dis-/charge rate of 1C in order to allow for a direct comparison with our previous work [16], despite the fact that this is not the theoretical capacity of NMC_{622} as active material for the positive electrode. For comparison, also cells with a liquid organic electrolyte (1M $LiPF_6$ in EC-DMC, 1:1 by weight; UBE) were assembled and tested. For the determination of the limiting current density, two-electrode pouch cells were assembled with the ionomer electrolyte membranes sandwiched between two lithium foils. The cells were kept in a climatic chamber at the corresponding temperature for 6 h prior to the application of a sweep rate of 0.025 mV s^{-1} using a Solatron 1400 CellTest system.

Results and discussion

To start with, Li|SI55%|NMC_{622} cells were subjected to galvanostatic cycling at 40 °C, setting the anodic cutoff voltage to 4.2 V in order to have a direct comparison with the results reported earlier for Li|SI55%|NMC_{111} cells [16]. Figure 2 a shows the dis-/charge profiles for the initial five formation

Fig. 2 Galvanostatic cycling of Li|SI55%|NMC_{622} cells with an anodic cutoff voltage of 4.2 V. **a** Dis-/charge profiles of the initial five cycles at 0.05C. **b** Plot of the specific discharge capacity and Coulombic efficiency vs. the cycle number with the C rate being increased to 0.5C after the first five cycles (temperature 40 °C)
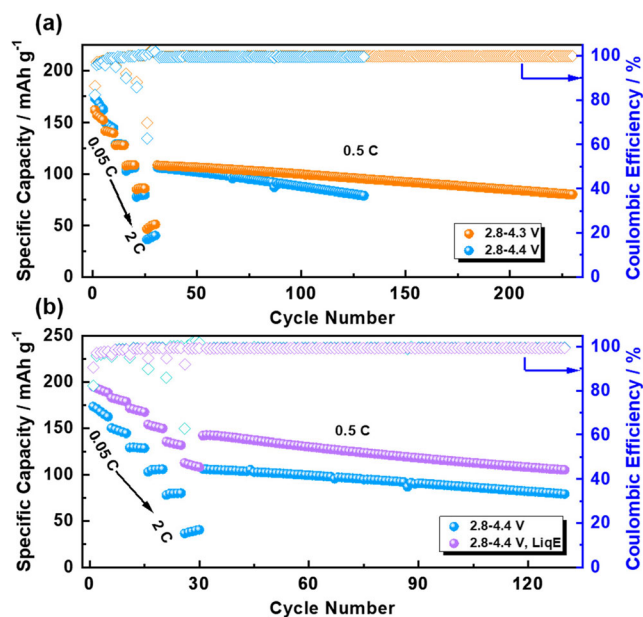

Fig. 3 a Rate capability and cycling stability test for Li|SI55%|NMC_{622} cells with an anodic cutoff voltage of 4.3 V (orange) and 4.4 V (turquoise). The dis-/charge rate was increased initially every five cycles from 0.05C to 0.1C, 0.2C, 0.5C, 1C, and 2C before subjecting the cells to constant current cycling at 0.5C for additional 200 cycles (in the case of 4.3 V) and 100 cycles (in the case of 4.4 V). In both cases, only the (reversible) discharge capacity is shown. The temperature was set to 40 °C. **b** Comparison of the rate capability and cycling stability of Li|SI55%|NMC_{622} cells (same as in (**a**)) and Li||NMC_{622} cells comprising a liquid organic electrolyte (1M $LiPF_6$ in EC/DMC, 1:1 by weight). For the latter test, the temperature was set to 20 °C

cycles at 0.05 C. The cell delivers a specific capacity of 157 mAh g^{-1}, while the first cycle Coulombic efficiency is about 85%. The subsequent long-term cycling (300 cycles performed at 0.5 C) is presented in Fig. 2b. The delivered capacity during the first cycles is 93 mAh g^{-1}, which slightly decreased upon cycling to stabilize at about 85 mAh g^{-1}. As a result, the capacity retention was 91.1%, 87.2%, and 81.1% after 100, 200, and 300 cycles, respectively. This impressive cycling stability considering the use of the Li metal electrode is accompanied by a very high average Coulombic efficiency of 99.95%, which is remarkably high as a result of the excellent compatibility of the ionomer electrolyte with Li metal.

In a next step, the cells were tested using higher upper cutoff voltage (4.3 V and 4.4 V: see Fig. 3a). The dis-/charge rate was initially varied from 0.05 up to 2C to investigate the rate performance and then kept constant at 0.5C in order to study the cycling stability. At 0.05C, the reversible specific capacity, i.e., the capacity obtained upon lithiation (discharge), increases from 157 mAh g^{-1} (@ 4.2 V) to 162 and 173 mAh g^{-1} when elevating the anodic cutoff voltage to 4.3 and 4.4 V, respectively. This trend is maintained increasing the C rate to 0.1C with slightly higher capacities for the Li|SI55%|NMC$_{622}$ cycled with an anodic cutoff of 4.4 V. When further increasing the dis-/charge rate to 0.2C, however, very similar capacities were obtained. Finally, at even higher C rates, the cells cycled with an anodic cutoff of 4.3 V showed higher capacities than the cell cycled with an anodic cutoff of

4.4 V. Precisely, specific discharge capacities of about 108, 86, and 49 mAh g^{-1} were obtained at 0.5C, 1C, and 2C, respectively, for an anodic cutoff of 4.3 V, while setting the anodic cutoff to 4.4 V led to capacities of around 103, 78, and 36 mAh g^{-1} at 0.5C, 1C, and 2C, respectively. After this rate capability test, the dis-/charge rate was set constantly to 0.5C to evaluate the general cycling stability. For an anodic cutoff of 4.3 V, the cells provided very stable cycling with about 73.8% capacity retention after 200 cycles (i.e., about 80 mAh g^{-1}). A very similar capacity retention of 74.4% was obtained for an anodic cutoff of 4.4 V, but after 100 cycles. These results suggest that the detrimental reactions occurring at the interface between the cathode and the ionomer electrolyte are more pronounced when elevating the anodic cutoff voltage to 4.4 V and that this effect outweighs the initially beneficial impact on the achievable specific capacity. This is in good agreement with a recent study on a very similar ionomer electrolyte system [18]. Remarkably, though, the capacity retention is slightly higher than for Li||NMC$_{622}$ cells comprising a common liquid organic electrolyte (1M LiPF$_6$ in EC/DMC), i.e., 74.4% vs. 74.0%, as depicted in Fig. 3b—despite the generally higher specific capacity across all dis-/charge rates, which is assigned to the substantially higher ionic conductivity (> 10 mS cm^{-1} at 20 °C^2 vs. < 1 mS cm^{-1} at 40 °C [16]) and potentially a better penetration of the electrolyte into the electrode's pores. This result indicates that the fading is, at least partially, related to the performance
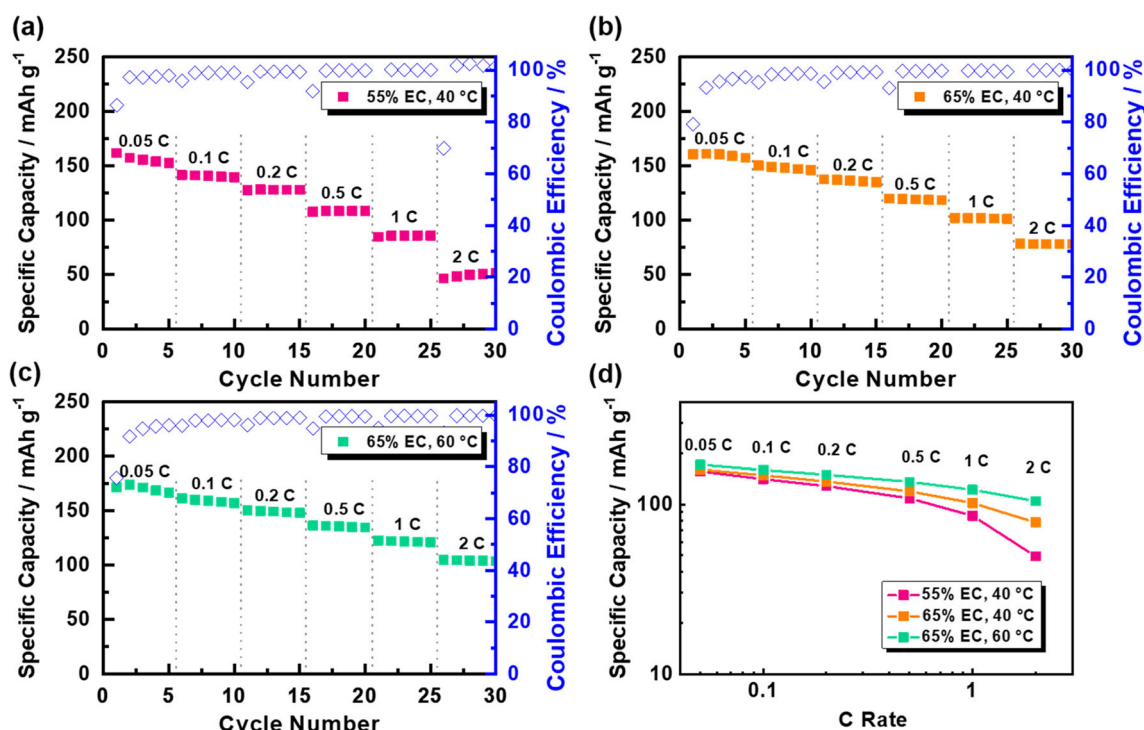

Fig. 4 Investigation of the impact of the EC content and ambient temperature on the rate capability of Li||NMC$_{622}$ cells. **a** Li|SI55%|NMC$_{622}$ at 40 °C (see also Fig. 3a). **b** Li|SI65%|NMC$_{622}$ at 40 °C. **c** Li|SI65%|NMC$_{622}$ at 60 °C. **d** Summarizing comparison of the results presented in **a**–**c**. The anodic cutoff was kept constant at 4.3 V, and only the discharge capacity is shown for clarity reasons

of the cathode-active material itself when setting the upper cutoff to 4.4 V and/or that the ionomer electrolyte offers the same oxidation stability of organic carbonate-based liquid electrolytes, in spite of the reportedly poor stability of ethylene carbonate at elevated potentials [19].

Following these results, 4.3 V was chosen as the anodic cutoff voltage for the subsequent investigation of the impact of the EC content and ambient temperature on the rate capability of Li|SIx%|NMC$_{622}$ cells (Fig. 4). In Fig. 4a, the evaluation of the rate capability for Li|SI55%|NMC$_{622}$ at 40 °C is shown again, serving as reference. The same test was subsequently applied for Li|SI65%|NMC$_{622}$ cells, i.e., employing a higher EC content in the ionomer membrane (Fig. 4b). This increase in EC concentration leads to higher capacities across all dis-/charge rates, particularly, at C rates above 0.5C. At 1C, for instance, the capacity increased from about 86 to 102 mAh g^{-1}, and at 2C, the capacity increased from around 49 to 78 mAh g^{-1}, corresponding to relative increases of about 19% and 58% at 1C and 2C, respectively. This superior rate capability is assigned to the improved ionic conductivity for SI65% compared with SI55% (around 1.2 mS cm^{-1} vs. 0.5 mS cm^{-1} at 40 °C [16]) and the enhanced limiting current density (1.3 mA cm^{-2} at 40 °C $vs.$ 1.2 mA cm^{-2} at 50 °C). In fact, when increasing the ambient temperature to 60 °C (Fig. 4c), a further rate capability improvement is observed—also at the lowest C rate of 0.05C, resulting in a specific capacity of about 171 mAh g^{-1} vs. 160 mAh g^{-1} for the Li|SI65%|NMC$_{622}$ cells. At 2C, the specific capacity was still around 104 mAh g^{-1}, which translates into a capacity retention of around 61% with regard to the capacity obtained at 0.05C—or an increase in capacity by 34% compared with the Li|SI65%|NMC$_{622}$ cells run at 40 °C. As a matter of fact, the enhanced kinetics is reflected also in an increased limiting current density with an increased temperature of around 1.5 mA cm^{-2} (vs. 1.3 mA cm^{-2} at 40 °C). The overall comparison of the rate capability when varying the EC content and elevating the ambient temperature is summarized in Fig. 4d, highlighting the stepwise improvement for an increased EC concentration and testing temperature.

Conclusions

Li||NMC$_{622}$ cells comprising single-ion–conducting SIx% as electrolyte provide excellent cycling stability for more than 300 cycles. Elevating the anodic cutoff voltage to 4.3 and 4.4 V leads to a slight decrease in cycling stability. However, the comparison with a common liquid organic electrolyte reveals that this decrease in cycling stability is related to either the cathode active material and/or the presence of EC, while the ionomer electrolyte is at least as stable as the liquid electrolyte at such elevated cutoff voltages. The rate capability, however, is lower for the Li||NMC$_{622}$ cells containing the ionomer electrolyte, though this can be substantially enhanced when increasing the EC content and/or applying elevated temperatures due to the increased ionic conductivities and limiting current densities at such conditions.

Compliance with ethical standards

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