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Enhancing Li⁺ Transport in NMC811 | Graphite Lithium-Ion **Batteries at Low temperatures by Using Low-Polarity-Solvent Electrolytes**

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Abstract: LiNi_xCo_yMn_zO₂ (x+y+z=1) | graphite lithium-ion battery (LIB) chemistry promises practical applications. However, its low-temperature ($\leq -20^{\circ}$ C) performance is poor because the increased resistance encountered by Li+ transport in and across the bulk electrolytes and the electrolyte/electrode interphases induces capacity loss and battery failures. Though tremendous efforts have been made, there is still no effective way to reduce the charge transfer resistance $(R_{\rm ct})$ which dominates low-temperature LIBs performance. Herein, we propose a strategy of using lowpolarity-solvent electrolytes which have weak interactions between the solvents and the Li⁺ to reduce R_{ct} , achieving facile Li⁺ transport at sub-zero temperatures. The exemplary electrolyte enables $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ graphite cells to deliver a capacity of $\approx 113 \text{ mAhg}^-$ (98% full-cell capacity) at 25°C and to remain 82% of their room-temperature capacity at $-20^{\circ}C$ without lithium plating at 1/3C. They also retain 84% of their capacity at -30° C and 78% of their capacity at -40° C and show stable cycling at 50°C.

Introduction

In addition to portable electronic devices, LIBs have been increasingly used to power electric vehicles (EVs) thanks to the significant cost reduction and energy density improvement in LIB technologies achieved in recent years. Application in EVs places the LIBs under requirements far more severe than consumer electronics: higher energy density for a longer driving range, improved safety, compatibility with fast charging (15-minute charge), as well as, a wider operating temperature range between -30° C and $+55^{\circ}$ C. The final two requirements have to this point proven to be the most urgent and challenging goals to realize for largescale EVs applications.^[1] The challenges of fast charging at room temperature and operating at low temperatures have a common origin related to the limitations in Li-ion (Li⁺) transport in and across the bulk electrolytes, and the electrode/electrolyte interphases (EEIs),^[2,3] which are strongly contingent upon the ionic conductivity of the electrolytes and the EEIs, as well as, resistance to desolvation of the Li⁺ from the electrolyte solvents.^[4-9] Thus, electrolyte engineering is central to the development of high-performance LIBs that are capable of fast charging and operating at low temperatures.^[10]

In the past few years, extensive efforts have been made towards improving the ionic conductivity of low-temperature electrolytes and modifying EEI components to optimize their stability and resistance against lithium metal anode-

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based LIBs.^[11-17] Fan et al. employed all fluorinated electrolytes which afforded a high discharging performance of lithium metal/LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ (Li | |NCA) batteries even at a low temperature of -85°C.^[11] Holoubek et al. reported 1 M lithium bis(fluorosulfonyl)imide) (LiFSI) in diethyl ether (DEE) electrolyte which showed good charging/ discharging performance at low temperatures with a lithium metal/sulfur (Li | |S) battery.^[12] Yang et al. used liquified gas as solvents and demonstrated excellent lithium-metal battery performance over a wide temperature range.^[17] However, advances in electrolyte design to enable low-temperature metal plating/stripping do not necessarily transfer well to graphite-based LIBs, given the need to realize much higher reversibility (coulombic efficiency (CE)>99.9%) of the electrode reaction and to avoid lithium plating on the graphite anode.^[18,19] Moreover, the strategies to reduce charge transfer resistance have barely been discussed and are not well-understood.

Most previous works on low-temperature graphite-based LIBs have generally focused on improving the low-temperature discharging performance only while charging is done at room temperature to avoid lithium plating on the graphite anode and ensure enough capacity retention because of the increased charge transfer resistance at low temperatures.^[20-22] Zhang et al. developed an EC-containing electrolyte that enables NMC811||Gr cells to discharge across a wide temperature range after charging at room temperature.^[21] Cho et al. reported an FEC-based electrolyte for $LiNi_{0.33}Co_{0.33}Mn_{0.33}\,|\,|graphite~(NMC111\,|\,|\,Gr)$ cells which could be discharged reversibly at low temperatures. However, when the cells were charged at -20 °C, lithium plating was observed.^[22] Additionally, to realize high energy density, the electrolyte needs to be stable to voltages > 4.5 V to accommodate the possible larger polarization on the cathode side at low temperatures. To the best of our knowledge, no specific electrolyte parameters/systems have yet been illustrated to effectively reduce R_{ct} and to enable NMC811||Gr cells to be charged and discharged at low temperatures while maintaining a good performance over a wide temperature range with high capacity retention and long cycle life.

To enable practical low-temperature NMC811 | Gr cells, electrolytes should satisfy all of the following requirements: 1) remain liquid at both low temperatures and high temperatures, 2) have high Li^+ conductivity of $> 10^{-3} \, \text{S} \, \text{cm}^{-1}$ and high transference number (>0.4), 3) remain oxidatively stable to voltages >4.5 V, 4) be capable of forming a thin but robust inorganic-rich solid electrolyte interphase (SEI) on the anode and cathode electrolyte interphase (CEI) on the cathode that are crucial for improving battery cycling stability and enhancing Li⁺ transport kinetics in EEIs, and 5) possess fast kinetics for Li⁺ desolvation from electrolytes, which is the main contributor to increased $R_{\rm ct}$ but is the hardest to realize. Herein, we introduce a simple electrolyte system, low-polarity-solvent electrolytes (LPSEs), which can fulfill all the above-mentioned properties very well. The system can generate inorganic-rich EEIs from anion decomposition promoted by high ratios of contact ion pairs (CIPs) and aggregates (AGGs) intrinsically and/or with the help of

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diluents which is beneficial for battery stability and Li⁺ transport in it.^[21,23] In the meanwhile, it specifically emphasizes the importance of weak ion-dipole interactions between solvent molecules and Li⁺ which is vital to reducing activation energy and resistance in the charge transfer process.

The viability of this electrolyte engineering approach to enhance Li⁺ transport kinetics and reduce battery resistance is illustrated by an electrolyte consisting of LiFSI lithium salt, ethyl methyl carbonate (EMC), and 1,1,2,2-tetrafluoro-3-(1,1,2,2-tetrafluoroethoxy) propane (TTE). EMC has a satisfactory temperature range from $-53\,^\circ\mathrm{C}$ to $110\,^\circ\mathrm{C}$ and a very small dipole moment ($\mu = 0.89 \text{ D}$) which suggests weaker ion-dipole interactions with Li+ compared with highly polar solvents (Table S1), promising enhanced kinetics and reduced R_{ct} for desolvation process.^[12] It also denotes the intrinsic ability to form partially dissociated salt domains with high ratios of CIPs and AGGs, which promote the formation of anion-derived inorganic-rich EEIs together with the extrinsic help of TTE diluent, providing good stability and Li⁺ transport property of EEIs. The designed electrolyte enables NMC811||Gr cells to operate across a wide temperature range from -40°C to 50°C with good stability and high capacity retention. The cells deliver high capacity retention of 113 mAh g^{-1} (out of 117 mAh g^{-1} , the specific energy is calculated based on the total mass of the anode + the cathode) at 25° C and 1/3C. Remarkably, they also maintain 81% of their room-temperature capacity at -20 °C at the same current of 1/3C without lithium plating and retain 84% of its capacity at -30°C and 78% of its capacity at -40°C. Electrochemical Impedance Spectroscopy (EIS) measurements show that the cells exhibit simultaneously reduced R_{ct} and Li⁺ transport resistance in EEIs, and smaller activation energies for these processes, demonstrating the great application potential of LPSEs in the future batteries.

Results and Discussion

Molecular Simulation-Validated Electrolyte Design Principle

Four electrolytes with different LiFSI-EMC and TTE components were prepared, and their ionic conductivities are summarized in Table S2. Since the formulation with the composition of LiFSI: EMC: TTE of 2:3.3:3.3 has the highest ionic conductivity of 1.1 mS cm⁻¹ at room temperature, it was selected for detailed characterization (denoted hereafter as the designed electrolyte, DE). Commercial electrolyte (denoted as the standard electrolyte, SE) of 1.0 M LiPF₆-EC: DMC (1:1 vol: vol) was also characterized for comparison.

Molecular dynamics (MD) simulations reveal the solvation structure of DE and corresponding binding energies of its solvates in detail. A presence of the TTE-rich and LiFSI(EMC)_{1.6}-rich domains is observed. A Li⁺ cation has the highest affinity to carbonyl oxygens Oc(EMC) followed by the oxygens from FSI⁻ (Figures 1a and 1b). The timeaveraged Li⁺ coordination shell (<3.0 Å) has 1.6 carbonyl

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Figure 1. a) Electrolyte structure of the 2.0 M LiFSI-EMC/TTE (designed electrolyte: DE) from MD simulations at 25 °C showing the TTE-rich and LiFSI (EMC)_{1.6} nano-domains. b) Radial distribution functions (RDFs), where Oc denotes carbonyl oxygen of EMC and EO(EMC) denotes non-carbonyl oxygens. c) The distributions of the solvates of the DE and 1.0 M LiPF₆-EC/DMC (vol:vol=1:1) (standard electrolyte: SE) and d) a distribution of the Li(FSI)_n AGGs in DE. Free energies of formation for the (TTE, EMC, FSI, Li) and (EC, DMC, PF₆, Li) solvates relative to the isolated solvents and anions in implicit solvent and Li⁺ in gas-phase for e) DE and f) SE electrolytes. A solvation model based on density (SMD) implicit solvation model with ε =20 for SE and ε =4.24 for DE was used to represent solvent that is not explicitly included in DFT calculations.

oxygens and 0.2 non-carbonyl oxygen from EMC, 2.7 O(FSI⁻), 0.11 F(TTE), and 0.03 F(FSI⁻). In agreement with FTIR shown in the following section, the majority (>97%)of carbonyl oxygens of EMC are coordinated to Li+, indicating an absence of free [not bound to Li⁺] EMC solvent that would be more susceptible to oxidation than Li^+EMC . The presence of 0.11F(TTE) coordinating a Li^+ and the absence of the Li-O(TTE) coordination reflects a weak interaction between the LiFSI(EMC)_{1.6}-rich domains and TTE diluent, which is consistent with the FTIR result.^[11] Analysis of the Li⁺(FSI, EMC, TTE) solvate populations shows that the distributions of AGGs, CIPs, and solventseparated ion pairs (SSIPs) are 74.39%, 23.52%, and 2.09% (Figure 1c), respectively. The local distributions of the FSIanions around Li^+ and Li^+ around the FSI⁻ anions are largely temperature-independent and show a preference for the Li(FSI)₂ and FSI(Li)₂ local coordination in ionic aggregates and the presence of large ionic aggregates with more than 100 ions (Figures S1a and S2b), validating the high ratios of CIPs and AGGs proposed in the previous section which is beneficial for the formation of anionderived electrode-electrolyte interphases at anode $\approx 1.6 \text{ V}$ and on cathode surfaces at a low state of charge (Figures S3 and S4a). Overall, 2% of Li⁺ are fully dissociated from FSI⁻ and diffuse two times faster than average Li⁺ (Figure S2c), while essentially no (<0.2%) of FSI⁻ are free (not coordinated to Li⁺), which results in the increased contribution of Li⁺ to ion transport from the positively charged Li⁺ (EMC)₄ complexes, compared with the FSI⁻ anion transport that relies on the structural diffusion with and within aggregates due to absence of free FSI⁻ and diffusion of ionic clusters. These differences in the anion and cation solvation are beneficial for cation transport and contribute to the increased t₊ observed experimentally for DE relative to SE.

In contrast, the lithium salt of the standard electrolyte is largely dissociated. Modeling predicts 60% of ions existing as SSIPs with a Li⁺ cation being preferentially solvated by carbonyl oxygens from EC followed by carbonyl oxygens of DMC and fluorines from PF_6^- as shown in Figure S5. The Li⁺ coordination numbers are 2.4 EC vs. 1.46 DMC and 0.43 PF_6^- at 25°C in accordance with previous reports.^[24] Unlike DE, where the majority of Li⁺ solvates are CIPs and AGGs

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(Figure S1a), in SE the SSIPs possess a population of 61.84% with Li⁺EC₃DMC and Li⁺EC₂DMC₂ being the dominant solvates followed by the LiPF₆·EC₂DMC, LiPF₆·EC·DMC₂ CIPs solvates (33.79%) (Figure S1b). The lower percentage of the AGGs and CIPs solvates does not favor the formation of the anion-derived interphases. The ubiquitous EC with high polarity (μ =4.61) in these clusters increases the ion-dipole interactions between the solvent molecules and the solutes, which therefore leads to higher resistance to Li⁺ desolvation, so to the charge transfer process. This solvent participation in the solvates is largely consistent with the relative binding energies of these solvents to Li⁺ in implicit solvent as shown in Figures 1e and 1f and is correlated with the experimental results.

To understand the Li⁺ desolvation free energies from various solvates in SE and DE electrolytes, the representative solvates were extracted every 5 ns from MD simulations followed by geometry optimization using density functional theory (DFT) calculations in implicit solvent (Figures 1e and 1f). In SE, the EC-dominating SSIP solvates, such as Li⁺ EC₄, and Li⁺EC₃DMC, have the highest free energy followed by CIPs solvates in accordance with the distribution of solvates extracted from MD simulations (Figure S1b). For DE, DFT calculations predict that the CIPs and AGGs solvates have much higher binding energy than SSIPs: Li⁺EMC₄ or Li⁺EMC₃, again in accordance with MD simulation results (Figure S1a). Focusing on the positively charged SSIPs solvates in SE and DE that are expected to be present at the negatively charged anode surface, Li⁺EC₄ and Li⁺EC₃DMC solvates are shown to have a higher binding free energy than Li^+EMC_n and Li^+EMC_3TTE (see Figures 1e and 1f). Only the DMC-rich Li⁺DMC₄ and Li⁺ DMC₄EC SSIP solvates in SE have Li⁺ desolvation free energy comparable to that for Li⁺EMC₄ SSIP in DE. The lower Li⁺ desolvation free energy for SSIPs in DE than in SE could contribute to lower interfacial resistance in DE vs. SE.

The self-diffusion coefficients and conductivity from MD simulations exhibit a near-Arrhenius behavior of the electrolyte and its components, which agrees with experimentally measured conductivity (Figure 2c and Figure S6) except for -20 °C for SE, where MD simulations predict conductivity of only the liquid phase component that is higher than overall conductivity of the semicrystalline SE electrolyte at this temperature.

At room temperature, DE electrolyte has two times higher concentration of charge carriers than SE but approximately 3 times slower diffusion of ions. An inverse Haven ratio that is also called ionicity is 0.15–0.21 for DE and 0.64– 0.8 for SE reflecting stronger ionic correlations in DE vs. SE. The stronger ionic correlations and slower ionic diffusion in DE vs. SE lead to lower conductivity of DE at room temperature but the absence of crystallization at lower temperatures results in higher conductivity for DE below -30 °C as shown in Figure 2.





Figure 2. Fourier-Transform Infrared Spectroscopy (FTIR) spectra of a) DE and its components, and b) SE and its components. c) The experimental and MD calculated temperature-dependent ionic conductivities of SE and DE. The record was taken each 10 °C from -40 °C to +60 °C. d) Differential Scanning Calorimetry (DSC) characterization of SE and DE electrolytes. The samples were cooled down to -84 °C and heated to 40 °C with a heating rate of 3 °C min⁻¹.

Experimentally-Measured Physicochemical Properties of the Electrolytes

The electrolyte solvation structures of DE and SE were studied by FTIR. The FTIR spectra of DE and its components (Figure 2a) show that the peak of carbonyl bond absorption shifts from 1747 cm⁻¹ to 1712 cm⁻¹ when 0.006 moles LiFSI is added into the 1 mL EMC (≈ 6 M based on the volume LiFSI-EMC solution), indicating that nearly all EMC solvent molecules are coordinated with at least one lithium ion.^[25,26] Further addition of TTE causes a blueshift of the signal from 1712 cm⁻¹ to 1717 cm⁻¹, which is believed to be a result of overall weakened coordination strengths between EMC and Li⁺ because of the interaction of the TTE with the solvates, reducing the binding energy further.^[14] This result is consistent with molecular simulations. The spectra of SE, DMC, and DMC-EC solvents are also measured as a benchmark (Figure 2b). The absorption peaks at 1811 cm⁻¹ and 1722 cm⁻¹ correspond to the carbonyl bond of EC and DMC coordinated with Li⁺, while a strong peak at 1753 cm⁻¹ is the signal of the uncoordinated carbonyl bond in DMC.^[25]

The ionic conductivity of the designed electrolyte and standard electrolyte in the temperature range of -40 °C to +60 °C was measured by using electrochemical impedance spectroscopy (EIS). As shown in Figure 2c, the ionic conductivity of SE rapidly drops below -20 °C, while the ionic conductivity of DE exhibits a gradual decrease across the whole temperature range of -40 °C to +60 °C. The sudden drop in the ionic conductivity of SE is attributed to the solidification of SE,^[15] which is inevitably induced by the high melting point of EC. The near-Arrhenius dependence of ionic conductivity versus temperatures of DE electrolyte indicates that there is no solidification. The explanations are

corroborated by a clear endothermic peak in SE around 0 °C and -28.7 °C in differential scanning calorimetry (DSC) measurements which also exhibits that DE maintains a liquid phase even at -84 °C (Figure 2d). Though the ionic conductivity of SE is higher than that of DE at temperatures > -10 °C (still $> 10^{-3}$ Scm⁻¹ at room temperature), it drops rapidly and is lower than that of DE at < -30 °C. Together with a high transference number of 0.537 that was experimentally measured for DE, these properties highlight the benefits of DE for low-temperature utilization.

The electrochemical stability window of DE was evaluated with cyclic voltammetry (CV) and linear sweeping voltammetry (LSV) at a scan rate of 0.1 mVs⁻¹ and was compared with SE. The reduction behaviors of the electrolytes were evaluated using graphite as the working electrode, while the anodic electrochemical stabilities were measured using aluminum (Al) as the working electrode. Figures S7 and S8 show the CV scan of Gr | |Li half cells and LSV of Al||Li half cells with DE and SE. The CV curve of the cell with SE shows a small reduction peak at ≈ 1.3 V, followed by two larger reduction peaks at ≈ 1.0 V and ≈ 0.65 V, which are assigned to the reduction of HF impurities and LiPF₆ contact ion pairs (CIPs), DMC and EC solvents, respectively.^[27,28] In comparison, the reduction peak of DE starts at a potential of ≈ 1.5 V, which can be attributed to the reduction of the LiFSI and LiF formation. This agrees with the DFT calculations in Figure S3 and previous work.^[29] Figure S8 shows the corrosion current density reaches $5 \,\mu\text{A}\,\text{cm}^{-2}$ at a potential of $\approx 4.75 \,\text{V}$ for the cell with SE while the LSV plot of the cell with DE has no obvious corrosion current until 5.0 V, demonstrating high anodic stability of DE.

Electrochemical Performance of Graphite Anodes and NMC811 Cathodes

The electrochemical performance of KS4 graphite anodes and NMC811 cathodes with DE were compared to those with SE at different temperatures by using Gr | Li $(0.5 \text{ mAh cm}^{-2})$ and NMC811 | |Li $(1.0 \text{ mAh cm}^{-2})$ half cells, respectively, to demonstrate the superior battery performance with LPSEs. KS4 graphite anodes and NMC811 cathodes experienced three formation cycles at a current density of 1/10 C at room temperature before further evaluations. As shown in Figure 3, the graphite anode at room temperature in DE at 3 C provides 91.3% of its capacity at 0.2 C (Figures 3a and S9a). In contrast, the capacity of an identical graphite anode in SE at 3 C only retains 86.6% of its capacity at 0.2 C (Figures 3c and S9e), indicating that the designed electrolyte enables the graphite anode to achieve a better rate performance than the standard electrolyte does. The superior rate performance of the graphite anode in DE can be attributed to the lower interfacial resistances on the graphite anode with DE than those of the cell with SE and a higher transference number of DE (0.537). Figure 3b shows the cycling stability and corresponding coulombic efficiency of graphite anodes in SE and DE at room temperature. The graphite anode with SE

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Figure 3. Electrochemical performance of Gr | |Li and NMC811 half cells with DE and SE. a) Rate performance and b) cycle stability of Gr | |Li half cells at room temperature at 1/3 C. c) Charging/discharging behavior and d) cycle stability of NMC811 | |Li halfcells at room temperature at 1/3 C. e) Rate performance and f) cycle stability of Gr | |Li half cells at -20° C at 1/3 C. g) Rate performance and h) cycle stability of Gr | |Li half cells at -20° C at 1/3 C. g) Rate performance and h) cycle stability of Gr | |Li half cells at -20° C at 1/3 C. g) Rate performance and h) cycle stability of graphite anodes is 0.5 mAh cm⁻², and the areal capacity of NMC811 cathodes is 1.0 mAh cm⁻²

shows a faster capacity decay than that in DE after 100 cycles, with a capacity retention of 79.3 % at 250 cycles which is consistent with a previous report,^[30] while the cell with DE has no obvious attenuation within the same number of cycles. DE is also compatible with the NMC811 cathode and the NMC811 | Li cell with DE shows a slightly better rate capability than that with SE (Figures 3c, S9b, S9d, and S9f). The cycling performance of the NMC811 cathode with DE is much better than that of the cell with SE (Figure 3d). The capacity retention of the NMC811 cathode with SE is 66.6 % after 100 cycles while the capacity retention of the NMC811 electrode with DE is 89.7 %, clearly demonstrating better compatibility between NMC811 cathodes and DE.

The merits of DE are also manifested at low temperatures for both graphite anodes and NMC811 cathodes. At -20 °C, the graphite anode in DE achieves a high capacity of 150 mAh g⁻¹ at a high rate of 4/5C and 307 mAh g⁻¹ at 1/3 C (Figures 3e and S10a), while an identical graphite anode in SE only provides 80 mAh g⁻¹ at the same rate of 1/3 C (Figure 3f). Additionally, Figure 3f shows the stable cycling performance of the graphite anode with DE at -20 °C with a stable charging/discharging capacity of ≈ 310 mAh g⁻¹ which corresponds to 83 % of its roomtemperature capacity after 250 cycles. The cell with DE also maintains a high CE throughout all cycles while the cell with SE does not, which indicates DE provides more adequate protection against electrode degradation and/or lithium plating.^[22] Figures 3g and S10b also show excellent rate performance of the NMC811 cathode with DE at -20 °C. The cell delivers high capacities of 129.5 mAh g⁻¹ at 2/3 C and 100.1 mAh g⁻¹ at 4/5 C, which correspond to 67 % and 52 % of its room-temperature capacity. Moreover, Figure 3h exhibits a better cycling performance of the NMC811 ||Li cell in DE than that in SE. The NMC811 cathode at -20 °C with DE retains a specific capacity of 155.8 mAh g⁻¹ after 100 cycles with a current density of 1/3 C. In contrast, the capacity of the NMC811 cathode with SE at -20 °C shows a fast capacity decay with 56.4 % of its initial capacity retained after 40 cycles.

Overall, the graphite anodes and the NMC811 cathodes with DE exhibit significantly higher rate capability and better long-term cycling stability than those with SE at both room temperature and -20 °C. The enhanced rate performance is believed to be associated with the increased transference number (0.537),^[31] weak Li⁺-solvent interaction, and thin and robust anion-derived inorganic-rich interphases which also lead to better stability of DE-containing cells.

NMC811 || Gr Full Cell Battery Performance

Due to the large surface area and the high content of carbon black, the irreversible capacity of the graphite electrode is somewhat high resulting in a low first-cycle coulombic efficiency in both DE (66.4%) and SE (68.4%). This irreversible capacity can be reduced by using graphite with a similar particle size with a low surface area (such as MCMB) or optimizing the electrode composition. Moreover, it can also be compensated by Li-rich **NMC811** $(Li_2[Ni_{0.8}Co_{0.1}Mn_{0.1}]O_2)^{[32]}$ (Figure S11a) or pre-lithiation of the graphite (Figure S11b). The cycling stability of NMC811||Gr full cells with an areal capacity of $1.0\,\mathrm{mAh\,cm^{-2}}$ was evaluated with SE and DE at room temperature, -20°C, and 50°C at a current of 1/3 C, and -30 °C, -40 °C as well after three formation cycles.

The NMC811 || Gr cell with DE also shows a high rate capability by maintaining 68% of its 0.1 C-capacity at 3 C, and 54% of its capacity at 4 C when only constant current charge (CCC) was conducted. When a constant voltage charge (CVC) procedure was added to the CCC step to make a complete 15-minute charge process, 70% of its 0.1 C-capacity at is delivered (Figure 4a) eventually. In comparison, the cell with SE shows less capacity retention by 7% at 1 C and 10% at 2 C, demonstrating that DE enables the better fast charging performance of NMC811 Gr cells than SE does. Figures 4b, S12a and S12c show that an NMC811 | Gr full cell with DE at 25 °C has better cycling stability than that with SE. At 200 cycles, the cell with DE retains 75 % of its initial capacity, while the capacity of the cell with SE quickly decays to only 59% of its initial value. The result is consistent with the performance of the graphite anodes and the NMC811 cathodes measured in half-cells. The charging-discharging profiles and cycling behaviors of NMC811||Gr cells with DE and SE being charged and discharged at -20°C are shown in Figures 4c, d, S12b and





Figure 4. The rate performance of the NMC811||Gr cell with DE at a) room temperature and c) -20 °C. Cycling performance of the NMC811||Gr cell with an areal capacity of 1.0 mAhg⁻¹ (N/P=1.15) in DE and SE at b) room temperature and d) -20 °C. e) Charging-discharging profile of the NMC811||Gr cell with DE with an areal capacity of 2.2 mAhg⁻¹ (N/P=1.15) at -20 °C. Rate capabilities of the NMC811||Gr cells with DE at f) -30 °C and g) -40 °C.

S12d. The NMC811 || Gr full cell with DE shows a high rate capability even at -20 °C (Figure 4c). The NMC811 || Gr cell at -20 °C maintains 91% of its room-temperature capacity (measured at 0.1 C) at 0.1 C, 88% capacity at 0.2 C and 53% capacity at 2/3 C. Furthermore, the capacity of the NMC811 || Gr cell with SE quickly drops to 30.9 mAh g^{-1} when it was cycled at -20 °C at 1/3 C. In contrast, the cell with DE maintains a specific capacity of $\approx 92.1 \text{ mAh g}^{-1}$ at -20 °C even after 250 cycles under the same testing conditions with no obvious capacity decay and a similar CE to that of the cell at room temperature, implying excellent stability and lithium plating-free cycling of the cells in DE at low temperatures.

Additionally, DE enables the NMC811||Gr full cell to operate with higher areal loading and across a wider temperature range from -40°C to 50°C. When the areal capacity of the cathode is 2.2 mAh cm^{-2} with the same N/P of ≈ 1.15 , the NMC811 || Gr cell with DE still maintains 68% of its room-temperature capacity at the current of 0.2 C at -20°C (Figure 4e). While the NMC811 ||Gr cell was charged/discharged at -30°C and -40°C at different current densities, high capacity retention can be kept as well. Figures 4f and 4g show that the NMC811||Gr cells with DE at 25°C deliver a capacity of 112.7 mAhg⁻¹ and 113.1 mAh g^{-1} at 0.1 C, which are consistent with all other abovementioned results. When the cell in DE was tested at -30 °C, 95.3 mAh g⁻¹ (84 % of its room-temperature capacity) at 0.1 C, 82.4 mAh g⁻¹ (73 %) at 0.2 C, 69.3 mAh g⁻¹ (61%) at 0.3 C and 62.6 mAh g^{-1} (55%) at 1/3 C is delivered; At -40°C, the NMC811||Gr cells deliver a capacity of 88.2 mAhg⁻¹ (78% of its room-temperature capacity) at 1/20 C and 61.7 mAg⁻¹ (55% of its roomtemperature capacity) at 1/10 C. However, the NMC811|| Gr cell with SE electrolytes cannot be charged/discharged at these temperatures. When the charging current density decreases from 1/10 C to 1/20 C, the discharging capacity of NMC811 | |Gr cell at -40 °C increases from 61.7 mAh g⁻¹ to 77.9 mAh g⁻¹ (69%) at 1/10 C (Figure S13), implying great adaptability of DE to low-temperature operations. The NMC811 | |Gr cells with DE can also stably operate at a high temperature of 50 °C retaining 91.1 mAh g⁻¹ capacity after 100 cycles, while the identical cell with SE shows a rapid capacity drop within the first 50 cycles (Figure S14).

DE enables NMC811||Gr full cells with an areal capacity of 1.0–2.2 mAh cm⁻² to achieve better performance than SE does with respect to rate capabilities and stability at both 25 °C and low temperatures. Moreover, it also delivers decent performance at -40 °C and +50 °C, signifying the latent potential of DE for use in practical electric vehicle batteries.

Electrochemical Behavior of Graphite Anodes and NMC811 Cathodes in NMC811||Gr Full Cells

The potentials and impedances of graphite and NMC811 electrodes in 1.0 mAh cm⁻² NMC811 ||Gr full cells were evaluated during charging/discharging processes using three-electrode pouch cells as shown in Figure S15. One of the graphite and NMC811 electrodes was used as the working electrode and the other acted as the counter electrode. A Li metal strip was employed as the reference electrode. The electrochemical impedance of the electrodes was measured at 25 °C and -20 °C at 50 % state of charge (SOC) after 10 activation cycles. Figures 5a–d show the impedances of the



Figure 5. EIS spectra of the NMC811 | |Gr with SE at a) RT and b) -20 °C, and with EIT1 at c) RT and d) -20 °C. Activation energies of e) the charge transfer process and f) lithium ions transport in the SEI of the graphite with DE and SE.

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graphite, the NMC811, and the NMC811 ||Gr full cell with SE and DE at both $25 \,^{\circ}$ C and $-20 \,^{\circ}$ C, respectively. The measured impedances of the NMC811 ||Gr full cell are similar to the sum of the impedance of the graphite anode and the NMC811 cathode in both SE and DE, indicating the three-electrode cells in Figure S15 can provide the real impedance of the anode and the cathode separately.

In the NMC811 || Gr full cell with SE, the impedance of the graphite anode is larger than that of the NMC811 cathode at both 25°C and -20°C, indicating that the graphite anode influences the NMC811||Gr full cell performance more which is in agreement with previously reported results.^[33] Additionally, impedances of both the graphite anode and the NMC811 cathode of the cell with SE significantly increase when the temperature is decreased to -20 °C (Figures 5a and b). In particular, the charge transfer resistance increases dramatically which is believed to be responsible for the poor low-temperature battery performance. In contrast, the impedances of the graphite anode and the NMC811 cathode for the cell with DE show much smaller increases. The impedance of the graphite anode of the cell with DE is similar to that of the NMC811 cathode at 25°C (Figure 5c) and is only slightly larger than that of the NMC811 cathode at -20° C (Figure 5d). The resistance to the charge transfer process and $\mathrm{Li^+}$ transport in EEIs is also very similar at both 25°C and -20°C, indicating the enhanced and well-matched transport kinetics of the sequential processes and between the cathode and the anode, which could therefore reduce the possibility for Li deposition on the graphite anode at -20 °C. The absence of Li plating on graphite anodes is verified by the potential of the graphite anode in the three-electrode NMC811 || Gr full cell with DE (Figure S16). It shows that the potential of the graphite is above 0.0 V even at a fully charged state at a current of 1/3 C at -20 °C. It is also reflected by the longterm cycling performance of Gr | |Li cells and NMC811 | |Gr cells during which all cells maintain a high CE through all cycles and no sudden voltage drops on the charging/ discharging curve are observed which can be assigned to the dissolution of the plated lithium into graphite, as illustrated above.^[22]

Previous resistance analysis shows that the graphite anode controls the low-temperature performance of NMC811||Gr full cells and the change of its resistance versus temperatures plays an important role. Therefore, with the assumption that all Li⁺ transport processes are thermally activated, the activation energy, which can be used to evaluate the energy barrier that determines the Li⁺ transport kinetics of these processes and the change rate of ln(1/R) vs. 1000/T was evaluated. EIS of the graphite anode in DE and SE was measured at different temperatures by using three-electrode pouch cells where a lithium foil and a lithium strip were used as the counter electrode and the reference electrode, respectively. The EIS of the graphite electrode at 50 % of SOC was measured across a temperature range from -10° C to 30° C (Figure S17). The EIS plot of graphite consists of two overlapped semicircles and a line in the low-frequency region. The high-frequency semicircle represents the impedance of Li⁺ transport in SEI and the



middle-frequency semicircle is attributed to the charge transfer process. The activation energies for the lithium ions transport in SEI and the charge transfer process were obtained by fitting SEI and charge transfer impedance versus different temperatures.^[34,35] As shown in Figures 5e and 5f, the activation energy of the charge transfer process of the graphite with DE (37.7 kJ mol⁻¹) is much smaller than that of the cell with SE (49.3 kJ mol⁻¹), and the activation energy of the lithium ions transport in SEI is also reduced in the cell with DE (50.3 kJ mol⁻¹) compared to that in the cell with SE (60.9 kJ mol⁻¹). This indicates enhanced kinetics for both the charge transfer process and lithium ions transport through SEI.

Charge transfer resistance is often associated with the desolvation energy of Li⁺ and many reports demonstrate the positive correlation between the desolvation energy and binding energy of Li⁺.^[4,17,34] Thus, the reduced charge transfer resistance of cells with DE can be attributed to the lower Li⁺ desolvation energy from the positively charged SSIP solvates in DE vs. SE discussed above (see Figures 1e and 1f). The weakened ion-dipole interactions between EMC and Li⁺ and the small coordination number of ≈ 1.64 as predicted by previous reports and simulations in the previous section validate the importance of the interactions between the solvent molecules and Li⁺.^[36,37] The significant decreases in resistance and activation energy of SEI are caused by the formation of thin inorganic-rich EEIs, as reported by others' work and illustrated in the following sections.^[23]

Graphite/Electrolyte Interphases

Interfacial resistance (charge transfer resistance and SEI resistance) of graphite anodes controls the electrochemical performance of NMC811 | | Gr full cells at low temperatures (Figures 5b and d) and its value is highly associated with the chemical components of the SEI.^[38,39] Since an inorganicrich SEI rich in LiF or Li2O has a lower electronic conductivity than an organic-rich SEI, the former is normally much thinner and more stable than the latter,^[40] which therefore reduces SEI resistance and enhances cycling stability. The thickness of the SEI formed on graphite in SE and DE was characterized using TEM. As shown in Figure 6a and Figure S18a, the pristine graphite has a clean surface. Figure 6b and Figure 6c show the TEM images of the graphite after 10 charging/discharging cycles in SE and DE, respectively. A \approx 3 nm-thick SEI can be identified on graphite cycled in SE (Figure 6b) due to the reduction of LiPF₆ and EC-DMC components. In comparison, a much thinner SEI of 1-2 nm is found on the graphite cycled with DE (Figure 6c). The thin SEI formed in DE is also much more robust than the SEI formed in SE during long-term charging/discharging cycles. Figures S18b and S18c exhibit the TEM images of the graphite anodes in SE and DE, respectively, after 100 charging and discharging cycles. It is observed that the SEI formed in SE grows from an initial thickness of 3 nm to 19 nm, while the thickness of SEI formed in DE only increases from 1–2 nm to \approx 7 nm. The



Figure 6. TEM images: a) pristine graphite, b) graphite cycled with SE, c) graphite cycled with DE, and XPS spectra of the graphite: d) O1s and e) F1s spectra of the graphite cycled with SE, and f) O1s and g) F1s spectra of the graphite cycled with DE. The graphite anodes for TEM were cycled 10 cycles while those for XPS were cycled 100 cycles.

SEI formed in DE is also more uniform than that formed in SE. The large difference in the SEI thickness and morphology could be attributed to the different chemical components of the SEI formed with these two electrolytes because the stability and electron-insulating properties of the SEI are the main determining factors to stop the growth of the SEI which therefore influences the following growth of it.^[41]

XPS measurements with Ar⁺ sputtering were conducted to analyze the chemical components of the SEI. Figure S19 shows the atomic ratio of different elements on the surface of pristine graphite and graphite anodes cycled with SE and DE. The atomic ratios of elements C, O, and F on the anodes with SE and DE are quite different. After 60 seconds of etching with Ar⁺, the F and O atomic ratios for the SEI formed with SE decrease from 42.7 % and 7.3 % to 27.6 % and 3.8%, respectively, while the C content of the SEI formed with SE increases from 50% to 68.8%, demonstrating the formation of organic-rich SEI on the graphite surface with SE. In contrast, the F content and O content of SEI formed on the graphite anode with DE are 45.8 % and 21 % respectively after etching for 60 s, and they maintain relatively high values of 40.5 % and 17.3 % after 600 seconds of etching. The C content of the SEI formed in DE is only 24.5% after etching for 60s and 35.1% at 600s, which are much smaller than those of the graphite anode cycled with SE. This implies a higher amount of organic content formed on the graphite surface with SE than with DE. The element atomic ratios could be further linked with organic and inorganic compounds to give us the relative content of these different types of compounds in the SEI. Figures 6d-g, S20a, S20b show the analysis results of the narrow scan of XPS. The SEI of graphite anodes cycled with SE consists of more organic components with a high concentration of C-C/C-H, C–O, C=O, and $Li_rPO_vF_z$ due to the decomposition of solvents and a small contribution from the reduction of $LiPF_6$ (Figures 6d and f). However, Figures 6e and g display that the SEI formed with DE is inorganic-rich consisting of a high concentration of LiF due to preferred salt reduction, supported by the DFT calculation results in Figure S3. This inorganic-rich SEI with low electronic conductivity can effectively insulate the anode from the electrolytes so that prevents the electrolytes from further decomposition, which therefore leads to an overall thin and stable SEI. This result is consistent with previously reported studies on electrolytes with similar compositions and demonstrates that an inorganic-rich SEI is beneficial for the low-temperature performance of LIBs.^[21]

NMC811/Electrolyte Interphases

CEI also plays an essential role in stabilizing the cathode, especially when the cathode has high nickel contents and is charged to a high voltage where the decomposition of the electrolytes generally occurs.^[42,43] Additionally, the ease of Li⁺ transport through the CEI also determines battery kinetics.^[44,45] The TEM and XPS measurements with the depth profile were conducted to study the CEI formed on cycled NMC811 cathodes with both SE and DE. Figures 7a and S21a show a clean surface on the pristine NMC811. The thickness of CEI on the NMC811 cathode cycled with SE in 10 cycles is ≈ 6 nm (Figure 7b). After 100 charging/discharging cycles in SE, the thickness of the CEI exhibits an increase to 17-36 nm (Figure S21b). However, the thickness of the CEI formed on NMC811 after 10 charging/discharging cycles in DE is only ≈ 2 nm (Figure 7c) and only increases to 13 nm after 100 charging/discharging cycles (Figure S21c). In addition, it shows a more uniform morphology. Both imply a robust CEI on the cathode and indicate a better Li⁺ conducting property in CEI.

The chemical components of the CEI were also characterized using XPS associated with Ar^+ sputtering. The relative ratios of organic to inorganic components in CEI



Figure 7. TEM images: a) pristine NMC811, b) NMC811 cycled with SE, c) NMC811 cycled with DE, and XPS spectra of the NMC811: d) O1s and e) F1s spectra of the NMC811 cycled with SE, and f) O1s and g) F1s spectra of the NMC811 cycled with DE. The NMC811 cathodes for TEM have cycled 10 cycles while those for XPS were cycled 100 cycles.

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can be calculated by combining Figures 7d-g and Figure S22. The relative ratio of organic species (C-O/C=O) to inorganic species in the CEI of the cathode formed with SE does not change at different CEI depths (Figures S22b and S23, Figures 7d and e) since the relative concentrations of F and O (Figure S22b) and the Li₂CO₃ and LiF signals (Figures 7d and e) of it are similar at different etching times. This indicates that the decomposition of the solvents and salts happens simultaneously in SE. In contrast, the relative percentage of organic compounds to inorganic compounds of CEI in DE decreases with increasing sputtering time (Figure S22c, Figures 7f and g), indicating that the inorganic CEI enriches the NMC811 surface cycled in DE. For example, the amounts of inorganic components (Li₂CO₃) (Figures 7f and S22b) and LiF (Figures 7g and S22c) increase with the sputtering time and therefore depth in the CEI developed in DE. The appearance of the Ni2p signal after 1440 seconds of sputtering time indicates that the sputtering is approaching the NMC811 surface (Figure S22d). This special distribution of the organic/inorganic components of the CEI formed in DE is attributed to the preferred decomposition of FSI- anion aggregates and possible sacrifice of TTE diluent compared to the solvent molecules, considering those are the main F sources in the electrolyte (Figure S4a).^[46] The decomposition of lithium salt and diluent gives a more organic/inorganic bilayer-like CEI in DE rather than the mosaic-like CEI in SE on NMC811 cathodes. The inorganic-rich inner layer of CEI in DE can suppress the further decomposition of the electrolyte and the growth of the CEI. The high interfacial energy of inorganic-rich CEI against NMC811 enables stabilization of the CEI during volume change of NMC811, thus achieving high cycling stability and good Li+ transport performance in it.

The formation of the inorganic-rich electrode/electrolyte interphases on both the anode and the cathode gives improved stability and enhanced Li⁺ transport kinetics in EEIs because of reduced electrode/electrolyte interphase resistance and reduced activation energy in the graphite anode. Together with the enhanced Li⁺ transport kinetics and decreased resistance in the charge transfer process by taking advantage of the highlight of the LPSEs, the designed electrolyte enables NMC811||Gr cells to deliver a stable cycling performance and great electrochemical kinetics under both fast charging and low temperatures conditions, making it promising for the use in practical power LIBs.

Conclusion

Low-polarity-solvent electrolytes (LPSEs) are introduced to enhance the Li⁺ transport kinetics both in and across the EEIs at low temperatures. The idea is illustrated with an exemplary electrolyte of 2.0 M LiFSI-EMC/TTE which enables the NMC811 ||Gr cell to operate in a wide temperature range from -40° C to 50°C, delivering a high capacity of 113 mAh g⁻¹ (out of 117 mAh g⁻¹ of the full cell) at 25°C and maintaining 81% of its room-temperature capacity at -20° C at a current density of 1/3 C without lithium plating. By analyzing the solvation structures, molecular interactions, electrode resistance, and the chemical components of EEIs via FTIR, molecular simulations, EIS, XPS, etc., the enhanced low-temperature performance is attributed to simultaneously reduced resistance and activation energies in both Li⁺ transport in EEIs and charge transfer process, which are caused by reduced desolvation energy and the formation of thin inorganic-rich interphases on both electrodes. These properties are further associated with the reduced ion-dipole interaction of the Li⁺ and solvents and intrinsically and/or extrinsically-enriched partially dissociated CIPs and AGGs domains in the electrolyte at a molecular level. The electrolyte engineering strategy proposed and demonstrated in the work sheds light on the relationship between the intermolecular interactions and Li⁺ transport kinetics and offers a new avenue to expand the service temperature range of LIBs while maintaining all other practical properties. It enables LIBs to work in extreme environments and holds promises for applications requiring power LIBs.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: Inorganic-Rich EEIs · Li-Plating Free · Low-Temperature Electrolyte · NMC811||Graphite · Weak Ion-Dipole Interactions

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Li-Ion Batteries

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C. Wang* _______ e202205967

Enhancing Li⁺ Transport in NMC811||Graphite Lithium-Ion Batteries at Low temperatures by Using Low-Polarity-Solvent Electrolytes



Low-polarity-solvent electrolytes (LPSEs) 1) enable the formation of the anionderived interphases on both electrodes and 2) have weak interactions between the solvent molecules and Li⁺, which provide fast Li⁺ transport kinetics and reduced resistance in both charge transfer process and Li⁺ transport in electrode/electrolyte interphases, achieving excellent battery performance under both fast-charge and low-temperature conditions.