Rate Performance of LiCoO$_2$ Half-cells Using Highly Concentrated Lithium Bis(fluorosulfonyl)amide Electrolytes and Their Relevance to Transport Properties

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Graphical abstracts

Highly concentrated Li[FSA] electrolytes in various solvents

- **Ohmic and Interfacial resistance**
  - GBL > DMC > DME > AN

- **Li ion mass transfer resistance**
  - GBL < AN < DMC < DME

Cell Voltage vs. Capacity

Discharge
Electrochemistry

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Abstract

For the rapid charge-discharge performance of Li-ion batteries (LIBs), ionic conductivity ($\sigma$) and Li ion transference number ($t_+$) are important parameters of electrolytes. Electrolytes with high $t_+$ alleviate the concentration polarization upon fast charge-discharge, and prevent the diffusion-limited mass transfer of Li$^+$ ions. Recent studies have suggested that certain highly concentrated electrolytes exhibit better rate performances than conventional organic electrolytes despite their lower $\sigma$. However, the relationship between the transport properties ($t_+$ and $\sigma$) of highly concentrated electrolytes and the enhanced rate performance of LIBs is yet to be elucidated. To evaluate the rate performance of LIBs with highly concentrated electrolytes in terms of transport properties, we investigated the discharge rate capability of LiCoO$_2$ (LCO) half-cells using highly concentrated lithium bis(fluorosulfonyl)amide (Li[FSA]) electrolyte in $\gamma$-butyrolactone (GBL), acetonitrile (AN), dimethyl carbonate (DMC), and 1,2-dimethoxyethane (DME) solvents. There was a remarkable solvent dependence of $t_+$, and the highest $t_{\text{Li}^+}^{\text{current}}$ of 0.67 was observed for GBL-based electrolyte measured using the very-low-frequency impedance spectroscopy (VLF–IS) method. The LCO half-cell with GBL-based electrolyte delivered higher discharge capacities than the cells with DMC- and DME-based electrolytes at high current densities. The improved rate performance in GBL-based electrolytes was attributable to enhanced Li$^+$ ion mass transfer derived from the high $t_{\text{Li}^+}^{\text{current}}$. We demonstrated the importance of $t_{\text{Li}^+}^{\text{current}}$ on the rate capability of LCO half-cells with highly concentrated electrolytes for high-rate battery performance.

Keyword: Li-ion batteries, Highly concentrated electrolytes, Rate performance, Transport properties
Introduction

In recent years, highly concentrated electrolytes (i.e., solvent-in-salt electrolytes) have attracted considerable attention as promising electrolytes for next-generation Li-ion batteries (LIBs), owing to their many advantages over conventional electrolytes, including wide electrochemical windows, high thermal stability, application to graphite electrodes without carbonate solvent and additives, stable cycling of lithium metal electrodes, and suppression of Al corrosion.

The rapid charge-discharge performance of LIBs is essential for accelerating the widespread use of electric vehicles and other energy storage technologies. In addition to ionic conductivity ($\sigma$), the Li-ion transference number ($t_+$), i.e., the ratio of the current carried by Li$^+$ ions to the total current, is also an important parameter of electrolytes to improve the battery rate performance. Electrolytes with high $t_+$ alleviate the concentration polarization upon fast charge-discharge, and prevent the diffusion-limited mass transfer of Li$^+$ ions. Newman et al. demonstrated the importance of the Li$^+$ ion transference number, showing that electrolytes with $t_+ = 1$ offer significant enhancement of material utilization, power, and energy density of lithium polymer batteries, particularly at high rates of discharge, even with low ionic conductivity. McCloskey et al. reported a finite element method based on Newman’s one-dimensional isothermal battery model to obtain suitable $t_+$ and $\sigma$ values for fast charging in LIBs using organic electrolytes with Li salt concentrations of 1 mol·dm$^{-3}$; they showed that electrolytes with higher Li$^+$ transference numbers would allow higher power densities and faster charging, even if their conductivities were substantially lower than those of conventional carbonate-based electrolytes. One may presume that highly concentrated electrolytes are not expected to improve high-rate battery
performance owing to their low ionic conductivities and high viscosities. However, in recent studies, a variety of concentrated electrolyte systems have been reported to exhibit better rate performances than conventional organic electrolytes.\textsuperscript{6,12-13} Nevertheless, the relationship between the enhanced rate performance of LIBs and the transport properties ($t_+$ and $\sigma$) of highly concentrated electrolytes is yet to be elucidated.

To evaluate the rate performance of LIBs with highly concentrated electrolytes, the discharge rate capability of LiCoO$_2$ (LCO) half-cells using highly concentrated lithium bis(fluorosulfonyl)amide (Li[FSA]) electrolyte in $\gamma$-butyrolactone (GBL), acetonitrile (AN), dimethyl carbonate (DMC), and 1,2-dimethoxyethane (DME) solvents and their relevance to the transport properties were studied. The chemical structures of the solvents are shown in Fig.1. Li$^+$ ions showed the highest diffusion rate among the ions and solvents in a highly concentrated GBL-based electrolyte, resulting in a high $t_+$ of 0.67, determined under anion-blocking conditions. The ion transport properties of the highly concentrated AN,\textsuperscript{6} DMC,\textsuperscript{2} and DME\textsuperscript{13}-based electrolytes were also studied for comparison, and LIBs with these electrolytes have reportedly shown improved rate performances. We investigated how the transport properties ($t_+$ and $\sigma$) affect the discharge performance of the LCO half-cell in these highly concentrated electrolytes.

**Figure 1.** Chemical structures of GBL, AN, DMC, and DME.
Experimental

Materials

Li[FSA] was purchased from Kishida Chemical Co. (Japan) and used as received. γ-Butyrolactone (GBL), dimethyl carbonate (DMC), and 1,2-dimethoxyethane (DME) were purchased from Kishida Chemical Co. (Japan), and were used as received. Acetonitrile (AN) was purchased from Wako Chemical Co. (Osaka, Japan). The sample electrolytes were prepared by mixing Li[FSA] and the solvent at an appropriate ratio in an Ar-filled glove box (VAC, [H\(_2\)O] < 1 ppm, [O\(_2\)] < 1 ppm).

Measurements

The ionic conductivity (\(\sigma\)) was determined using an impedance analyzer (VMP-3, Biologic), in the frequency range from 500 kHz to 1 Hz, with a voltage amplitude of 10 mV. Two platinized platinum electrode cells (CG-511B, TOA Electronics) were used for the conductivity measurements, and the cell constant was determined using a 0.01 M KCl aqueous solution at 25 °C. The density (\(d\)) and viscosity (\(\eta\)) were determined using a Stabinger viscometer (SVM 3000, Anton Paar), and the Li salt concentration (\(c\)) was determined from the density value at 30 °C and the molecular weight of the electrolytes.

Pulsed-field gradient nuclear magnetic resonance (PFG–NMR) measurements were conducted to determine the self-diffusion coefficients of solvent, Li\(^+\), and [FSA]\(^-\) using a bipolar pulse-pair longitudinal eddy current delay (BPP–LED) pulse sequence with sinusoidal PFG.\(^{14,15}\) The experimental details for PFG-NMR are described elsewhere.\(^{20}\)
Raman spectra were recorded using a Raman spectrometer with a 785-nm laser (NRS-4100, JACSO); the instrument was calibrated using a polypropylene standard. The spectroscopic resolution was 4.6 cm\(^{-1}\). The samples were sealed in a capillary tube, and their temperature was controlled using a Peltier microscope stage (TS62, INSTEC) with a temperature controller (mk1000, INSTEC).

Two different Li ion transference numbers were determined either by the very-low-frequency impedance spectroscopy (VLF–IS) or from the self-diffusion coefficients obtained from PFG–NMR. The VLF–IS experiments were performed using an Li symmetric cell, as reported by Wohde et al.\(^{16}\) A porous glass filter paper (Advantec, GA55, 17 mm in diameter), impregnated with the liquid electrolyte, was placed between two Li foil electrodes (Honjo Metal, 16 mm in diameter) in a 2032-coin-type cell. Impedance spectra were recorded in the frequency range from 0.1 mHz to 1 MHz with a perturbation voltage amplitude of 10 mV for measuring the finite diffusion impedance of Li\(^+\) ions, using an impedance analyzer (Modulab XM, Solartron Analytical). Impedance measurements were preliminarily performed every hour prior to the VLF–IS experiments to confirm the stabilization of the Li electrode/electrolyte interface.

Charge-discharge tests were conducted on [Li metal anode | electrolyte | LiCoO\(_2\) cathode] cells with different electrolytes. For the LiCoO\(_2\) electrode, LiCoO\(_2\) powder (Nippon Chemical Industrial Co., Japan), acetylene black (AB, Denki Kagaku Kogyo, Japan), and poly(vinylidene fluoride) (PVDF, Kishida Chemical Co., Japan) were used as the active material, conduction supporting agent, and binder, respectively. A slurry of the above-mentioned materials (mass ratio = 80/10/10) with N-methylpyrrolidone (NMP, Kanto Chemical Co., Japan) was spread on an Al foil current collector and
dried at 80 °C. The cathode sheet was cut into a circle with a diameter of 16 mm. The cells were assembled in a 2032-type coin cell in an Ar-filled glove box. Glass fiber separators (GA-55, Advantec) were also used. Galvanostatic charge-discharge measurements were performed using an automatic charge-discharge instrument (HJ1001SD8, Hokuto Denko) at 30 °C. The cutoff potentials were set at 3.0 and 4.2 V. The specific capacity of the cell was calculated on the basis of active material loading (4.1–4.4 mg·cm⁻² LCO). In rate performance, charge current density was always 0.2 mA·cm⁻², and the discharge current density varied from 0.2 mA·cm⁻² to 10 mA·cm⁻² per 4 cycles.

The electrolyte ohmic resistance ($R_{\text{ohm}}$) and interfacial resistance ($R_{\text{interface}}$) were measured using the AC impedance method on a [Li metal anode | electrolyte | charged LiCoO₂ cathode] cell. The cells were different from those used for determining the rate performance. The charged LiCoO₂ cathodes were prepared by three charge-discharge cycles, followed by charging to 4.2 V, and the impedance spectra of the charged cell were collected with a sinusoidal alternating voltage amplitude of 10 mV over the frequency range from 100 kHz to 100 mHz.

Results and Discussion

Transport properties and coordination structure

In Fig. 2, the ratio of the self-diffusion coefficients of the solvent and Li⁺ ion ($D_{\text{sol}}/D_{\text{Li⁺}}$), and those of the [FSA]⁻ anion and Li⁺ ion ($D_{\text{FSA}}/D_{\text{Li⁺}}$) of the electrolytes are plotted versus the Li salt concentration, c. The numerical data of the diffusion coefficients and other physicochemical properties (including $\eta$, $d$, $c$, and $\sigma$ at 30 °C) for each electrolyte are shown in Tables S1–S4. At $c \approx 1$ mol dm⁻³, the self-
diffusion coefficients followed the order: \( \text{Li}^+ \text{ ion} < \text{anion} < \text{solvent} \) in all the electrolytes. Despite the small size of the \( \text{Li}^+ \) ions, it was found that \( D_{\text{Li}} < D_{\text{sol}} \) due to the larger hydrodynamic radius of the ‘solvated’ \( \text{Li}^+ \) ions, in reference to the Stokes–Einstein relationship. The same trend (i.e., \( D_{\text{sol}}/D_{\text{Li}} > 1 \)) was also observed even at concentrations up to \( c \approx 6 \text{ mol} \cdot \text{dm}^{-3} \) for the AN-, DME-, and DMC-based electrolytes. \( D_{\text{FSA}}/D_{\text{Li}} \) became close to or slightly lower than 1 in the high-concentration region except in the GBL-based electrolytes, implying that \( \text{Li}^+ \) ions diffused in the form of ion pairs. In our previous study, we found that the same held true for highly concentrated electrolytes of lithium bis(trifluoromethanesulfonyl)amide (Li[TFSA]) in tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), and dimethyl sulfoxide (DMSO) solvents. \(^{17-18}\)

![Figure 2](image)

**Figure 2.** The ratios of the self-diffusion coefficients, (a) \( D_{\text{sol}}/D_{\text{Li}} \) and (b) \( D_{\text{FSA}}/D_{\text{Li}} \) of Li[FSA] in GBL-, AN-, DMC-, and DME-based electrolytes at various Li salt concentration at 30 °C.

In contrast, in GBL-based electrolytes, \( \text{Li}^+ \) ions diffuse faster than the solvent and the anion in the high-concentration region (\( c \approx 6 \text{ mol} \cdot \text{dm}^{-3} \)). This unique \( \text{Li}^+ \) ion diffusion behavior is not interpreted by the physical diffusion mechanism based on the Stokes–Einstein rule, and agrees well with our recent observations for sulfolane-, \(^{12,19}\) keto ester-, \(^{20}\) and dinitrile-based concentrated electrolytes. \(^{21}\)
these highly concentrated electrolytes, a solvent molecule coordinated to two different, neighboring Li$^+$ ions, forming a chain-like Li-ion coordination structure consisting of solvent bridges (−Li$^+$−solvent−Li$^+$−) and aggregated ion pairs (AGG, Li$_i$X$_j$(c$^e$,y$^i$), where X denotes counter anions). The polymeric Li-ion coordination structure percolating through the liquid electrolytes is considered to serve as an efficient Li$^+$ ion transport pathway, enabling the fastest Li$^+$ ion diffusion by the Li$^+$ ion hopping/exchange mechanism.

Likewise, the highly concentrated GBL-based electrolyte should have a unique Li-ion coordination structure, similar to the other highly concentrated electrolytes, contributing to the fastest Li ion diffusion. Raman spectra of Li[FSA]/GBL solutions over the wavenumber range 650–720 cm$^{-1}$ revealed a band assigned to a ring-stretching mode of GBL (Fig. 3a).$^{22}$ As detected in the GBL solvent, the band at 678.5 cm$^{-1}$ corresponded to uncoordinated (free) solvent species. The intensity of this band decreased with increasing Li[FSA] concentration, and another band emerged at ∼689 cm$^{-1}$, yielding a clear isosbestic point at ∼683 cm$^{-1}$. The new peak is attributed to GBL bound to a Li$^+$ ion via its carbonyl oxygen.$^{23}$ At the Li[FSA]/GBL ratio of 1/1 (c ≈ 6 mol dm$^{-3}$), the band at 678.5 cm$^{-1}$ became significantly weaker in intensity, whereas the band at ∼689 cm$^{-1}$ became dominant. This suggests that the uncoordinated GBL molecules are nearly absent, and almost all the GBL was coordinated to Li$^+$ ions. We have not obtained any decisive evidence for the solvent-bridged structure from Raman spectra; however, in a recent study on the Na[FSA]/GBL=1/1 system, the solvent-bridged structure, in which the carbonyl site of the GBL molecule coordinates to two different Na$^+$ ions, was identified in the single-crystal structure and was suggested to be partially retained in the liquid state.$^{24}$ Analogous
to the Na system, the solvent-bridged Li-ion coordination structure may also exist at the Li[FSAn]/GBL ratio of 1/1.

A Raman spectral peak in the range 700–800 cm\(^{-1}\) was assigned to the S–N stretching vibration of [FSAn]\(^-\), and the peak position shifted to a higher wavenumber with increasing Li[FSAn] concentration (Fig. 3b). This shift is often observed in concentrated electrolytes with sulfonlamide-based alkali metal salts and is attributed to the increased interaction between the alkali metal cation and the amide anion.\(^{25}\) The Raman band at \(\sim 722\) cm\(^{-1}\) was assigned to free [FSAn]\(^-\) anions and/or [FSAn]\(^-\) anions within a solvent-separated ion pair (SSIP) without direct coordination to a metal cation. The bands at \(\sim 735\) cm\(^{-1}\) and \(\sim 752\) cm\(^{-1}\) were assigned to [FSAn]\(^-\) within the contact ion pair (CIP) and AGG, respectively.\(^{25-26}\) The observed shift to higher wavenumbers is indicative of complexation between [FSAn]\(^-\) and Li\(^+\), implying that AGG forming a chain-like Li-ion coordination structure with solvent molecules may also exist in the highly concentrated region.
The Li-ion coordination structures in DMC-, AN-, and DME-based concentrated electrolytes have already been reported.\textsuperscript{2,6,13} Monodentate ligand solvents, such as DMC and AN, and a bidentate ligand solvent, such as DME, have been reported to coordinate solely to one Li\textsuperscript{+} ion, but were not arranged in solvent-bridged structures even at high concentrations. The counter anions were found to interact with the Li\textsuperscript{+} ions, forming CIPs and AGGs in each electrolyte, similar to the highly concentrated GBL-based electrolyte.

**Li\textsuperscript{+} transference number**

The Li-ion transport properties under the influence of electric potential gradients and concentration gradients play an important role in determining the battery performance. To evaluate the Li\textsuperscript{+} ion transport properties, Li\textsuperscript{+} transference numbers have been used, and many different measurement methods have been applied.\textsuperscript{16, 27-29} One of the popular methods relies on self-diffusion coefficient
measurements using PFG–NMR. The Li$^+$ transference number is simply determined as the ratio of the self-diffusion coefficients of Li ions ($D_{\text{Li}^+}$) to the sum of those of the cations ($D_{\text{Li}^+}$) and anions ($D_{\text{anion}}$):

$$t_{\text{Li}^+}^{\text{NMR}} = \frac{D_{\text{Li}^+}}{D_{\text{Li}^+} + D_{\text{anion}}} \quad (1)$$

For conventional electrolytes such as the LiPF$_6$/carbonate solvent, $t_{\text{Li}^+}^{\text{NMR}}$ has been reported to be 0.3–0.4. However, this method assumed that the ions were completely dissociated and moved independently, similar to an ideal electrolyte solution at infinite dilution. Therefore, the thus-obtained $t_{\text{Li}^+}^{\text{NMR}}$ may not be meaningful for evaluating the ionic transport properties of highly concentrated electrolytes, in which the interionic interactions and mutual correlations of ion motions are significant.

In this study, we adopted the very-low-frequency impedance spectroscopy (VLF–IS) method to estimate the Li$^+$ transference number ($t_{\text{Li}^+}^{\text{current}}$) as follows:

$$t_{\text{Li}^+}^{\text{current}} = \frac{R'_{\text{ohm}}}{R'_{\text{ohm}} + R'_{\text{diffusion}}} \quad (2)$$

where $R'_{\text{ohm}}$ is the electrolyte ohmic resistance, and $R'_{\text{diffusion}}$ is Li$^+$ ion mass transport resistance in an Li symmetric cell. Although $t_{\text{Li}^+}^{\text{current}}$ is equivalent to the true Li$^+$ ion transference number only for dilute and completely dissociated electrolytes, this value can be determined for any sample unless the electrolytes severely decompose at the Li metal electrode. Moreover, $t_{\text{Li}^+}^{\text{current}}$ is the value measured under anion-blocking conditions, similar to the saturation in LIBs; therefore, this value would be practically useful for characterizing the ionic transport properties of battery electrolytes.

The Li$^+$ transference numbers ($t_{\text{Li}^+}^{\text{current}}$, $t_{\text{Li}^+}^{\text{NMR}}$) and physicochemical properties of highly concentrated GBL-, DMC-, AN-, and DME-based electrolytes are listed in Table 1. The molar ratio
of each electrolyte was close to that at the saturation point at 30 °C: Li[FSA]:GBL=1:1, Li[FSA]:AN=1:1.5, Li[FSA]:DMC=1:1, and Li[FSA]:DME=1:0.8. The impedance spectra (R_{ohm} and R_{diffusion}) for an Li symmetric cell are given in Fig. S1 and Table S5. The value of $t_{Li^+}^{\text{NMR}}$ exceeded 0.5 in each electrolyte, and the highest value (0.6) was obtained for the GBL-based electrolyte. The difference of $t_{Li^+}^{\text{current}}$ was more remarkable than that of $t_{Li^+}^{\text{NMR}}$. The value of $t_{Li^+}^{\text{current}}$ followed the order GBL > AN ~ DMC > DME. The minimum and maximum $t_{Li^+}^{\text{current}}$ values (0.29 and 0.67, respectively) were obtained for the DME-based and GBL-based electrolytes, respectively.

The solvent effects on the $t_{Li^+}^{\text{current}}$ measured under anion-blocking conditions of highly concentrated electrolytes have been elucidated in previous molecular dynamic simulations and experimental studies.\textsuperscript{28, 30} It has been reported that concentrated electrolytes with longer oligoether solvents like tetraglyme (G4) show much lower $t_{Li^+}^{\text{current}}$ than electrolytes with shorter oligoether solvents like DME, even at similar Li salt concentrations. The molecular origin of the difference in $t_{Li^+}^{\text{current}}$ was related to the residence time of solvents to Li$^+$ ions: the residence time was longer for more strongly coordinating, multidentate G4, resulting in a lower value of $t_{Li^+}^{\text{current}}$. The studies on the dynamic ion correlations suggest that pronounced anti-correlations of the ion motions (especially for cation–cation motions of the long-lived [Li(G4)]$^+$ complex cations) due to the constraint of momentum conservation of the ions are responsible for the extremely low $t_{Li^+}^{\text{current}}$.\textsuperscript{28, 30} The solvent dependence on $t_{Li^+}^{\text{current}}$ in this study corroborated the results reported above. The residence times of the monodentate GBL, AN, and DMC were shorter than that of bidentate DME. The momentum exchange of the ions can be remarkably compensated in the monodentate-based electrolytes with more frequent
solvent exchange. Therefore, the anti-correlations of ion motions can be less-pronounced in the GBL-, AN-, and DMC-based electrolytes, and they show higher \( t_{\text{Li}^+}^{\text{current}} \) values than the DME-based electrolyte. We previously reported a remarkably high \( t_{\text{Li}^+}^{\text{current}} \) value of 0.7–0.8 for SL-based concentrated electrolytes, in association with the fastest \( \text{Li}^+ \) ion diffusion behavior and the solvent-bridged \( \text{Li}^- \)ion coordination structure.\(^{31}\) Given the unusual \( \text{Li}^+ \) ion diffusion behavior (Fig. 2), the solvent-bridged \( \text{Li}^- \)ion coordination structure speculated from Raman spectra (Fig. 3), and the crystalline structure of the Na counterpart, a similar scenario can be envisaged for the GBL-based concentrated electrolyte displaying the highest \( t_{\text{Li}^+}^{\text{current}} \) value of 0.67.

**Table 1.** Viscosity (\( \eta \)), density (\( \rho \)), \( \text{Li}[^{\text{FSA}}] \) concentration of (\( c \)), ionic conductivity (\( \sigma \)), and lithium transference numbers (\( t_{\text{Li}^+}^{\text{current}}, t_{\text{Li}^+}^{\text{NMR}} \)) of \( \text{Li}[\text{FSA}] \) with GBL, DMC, AN, DME-based electrolytes at 30 °C.

| Electrolyte     | \( \eta \) / mPa s | \( c \) / mol dm\(^{-3} \) | \( \sigma \) / mS cm\(^{-1} \) | \( t_{\text{Li}^+}^{\text{NMR}} \) \( / - \) | \( t_{\text{Li}^+}^{\text{current}} \) \( / - \) |
|-----------------|---------------------|-----------------|-----------------|-----------------|-----------------|
| \( \text{Li}[\text{FSA}]:\text{GBL}=1:1 \) | 586                 | 5.98            | 0.76            | 0.60            | 0.67            |
| \( \text{Li}[\text{FSA}]:\text{DMC}=1:1.1 \) | 376                 | 5.74            | 0.88            | 0.51            | 0.35            |
| \( \text{Li}[\text{FSA}]:\text{AN}=1:1.5 \) | 109                 | 5.93            | 3.4             | 0.53            | 0.33            |
| \( \text{Li}[\text{FSA}]:\text{DME}=1:0.8 \) | 213                 | 5.82            | 1.7             | 0.51            | 0.29            |

**Discharge rate performance**

In this section, the discharge rate performance of the LCO half-cell with highly concentrated electrolytes is discussed in terms of the ionic transport properties (\( \sigma \) and \( t_{\text{Li}^+}^{\text{current}} \)). The discharge curves at different current densities for each electrolyte are presented in Fig. S2. Fig. 4 shows the discharge capacities per cycle for the electrolytes. At current densities lower than 2 mA·cm\(^{-2} \), all the cells showed discharge capacities of \(~140\) mA·h·g\(^{-1} \), which is close to the theoretical capacity of LCO.
With a further increase in the current density, the discharge capacities of the cells gradually declined. The GBL- and AN-based electrolytes exhibited discharge capacities greater than 110 mA·h·g⁻¹ (78% capacity retention) even at a high current density of 8 mA·cm⁻², while the capacity was severely reduced to ~75 mA·h·g⁻¹ (54% capacity retention) for the DMC- and DME-based electrolytes at the same current density.

![Figure 4](image-url). Cycle performance of discharge capacity with different current densities ranging from 0.2 cm⁻² to 10.0 cm⁻² at 30 °C with Li[FSO₄]:GBL=1:1 (red), Li[FSO₄]:AN=1:1.5 (blue), Li[FSO₄]:DME=1:0.8 (purple), and Li[FSO₄]:DMC=1:1.1 (green).

The discharge voltage profiles at a high current density of 8 mA·cm⁻² (Fig. 5) clarify the effect of ion transport properties on the discharge behavior of the LCO half-cells. In the AN-based electrolyte ($\sigma = 3.4$ mS cm⁻¹, $t_{\text{Li}^+}^{\text{current}} = 0.33$), the voltage drop in the early stage of discharge was the lowest, and the voltage gradually decreased to reach the lower voltage limit of 3 V, showing the high discharge capacity of 110 mA·h·g⁻¹. In the GBL-based electrolyte ($\sigma = 0.76$ mS cm⁻¹, $t_{\text{Li}^+}^{\text{current}} = 0.67$), the initial voltage drop was the largest among the electrolytes studied; however, the discharge plateau was
markedly extended to a discharge capacity similar to that for the AN-based electrolyte. In contrast, in the DME- ($\sigma = 1.7$ mS·cm$^{-1}$, $t_{Li^+}^{\text{current}} = 0.29$) and DMC- ($\sigma = 0.88$ mS·cm$^{-1}$, $t_{Li^+}^{\text{current}} = 0.35$) based electrolytes, even though their initial overvoltage was lower than that for the GBL-based electrolyte, the cells showed a steeper voltage drop in the middle and end of the discharge profile.

The total overvoltage in the discharge profiles arises from the electronic and ionic resistances ($R_{\text{ohm}}$), the interfacial resistance, including charge transfer resistance at the electrodes, the solid electrolyte interphase resistance (SEI) ($R_{\text{interface}}$), and Li$^+$ ion mass transport resistance ($R_{\text{diffusion}}$). To examine the $R_{\text{ohm}}$ and $R_{\text{interface}}$ of the LCO half-cells, the impedance spectra of the [Li metal anode | electrolytes | charged LiCoO$_2$ cathode] cell were recorded using the AC impedance method. The obtained Nyquist plots were fitted using the equivalent circuit shown in the inset of Fig. S3. The fitting results of $R_{\text{ohm}}$ and $R_{\text{interface}}$ are summarized in Table S6. The interfacial resistance ($R_{\text{interface}}$) represents the total charge

![Galvanostatic discharge curves](image.png)

**Figure 5.** Galvanostatic discharge curves of [Li metal anode | electrolyte | LiCoO$_2$ cathode] cells at 8 mA cm$^{-2}$ at 30 °C with Li[FSA]:GBL=1:1 (red), Li[FSA]:AN=1:1.5 (blue), Li[FSA]:DMC=1:1.1 (green), and Li[FSA]:DME=1:0.8 (purple).
transfer resistance at the LiCoO$_2$ cathode, Li metal anode, and the resistance of the SEI layer. The semicircles in the high-frequency range can be assigned to the charge transfer process at the Li anode and the resistance of the SEI layer, because semicircles were observed for the Li symmetric cell over a similar frequency range (Fig. S1). The other semicircles in the low-frequency region were derived from the charge transfer process at the LCO cathode.

The initial overvoltage was predominantly caused by ohmic resistances originating from the contributions of the ionic resistance of the electrolyte and the electronic resistances of the LCO and Li electrodes and the contact resistance between the electrodes and current collectors. Given the data acquisition rate of the charge-discharge instrument, the initial overvoltage can also be affected by $R_{\text{interface}}$. Indeed, there is a good relationship between the total resistances of $R_{\text{ohm}}$ and $R_{\text{interface}}$ and the initial overvoltage of the cells (Fig. S4). The values of $R_{\text{ohm}}$ followed the order: GBL > DMC > DME > AN. The highest initial polarization was attributed to the lowest ionic conductivity of the GBL-based electrolyte. The values of $R_{\text{interface}}$ followed the order: GBL > DME > DMC > AN. Although the cause for the observed difference in $R_{\text{interface}}$ needs further investigation, the larger value of $R_{\text{interface}}$ for the GBL-based electrolyte is possibly due to the slow Li$^+$ ion solvation/de-solvation kinetics in the electrolyte with the highest viscosity. Not surprisingly, the smallest total resistance of $R_{\text{ohm}}$ and $R_{\text{interface}}$ for the AN-based electrolyte was responsible for the highest capacity. However, it is difficult to explain the higher capacity of the GBL-based electrolyte compared to the DMC- and DME-based electrolytes in terms of the total resistance of $R_{\text{ohm}}$ and $R_{\text{interface}}$. The significantly high value of $i_{\text{Li}^+}^{\text{current}}$ suggests that Li ion mass transfer is more enhanced in the GBL-based electrolyte, leading to the high capacity.
despite the highest total resistance of $R_{\text{ohm}}$ and $R_{\text{interface}}$.

Although the actual mass transfer resistance, $R_{\text{diffusion}}$, of the LCO half-cell was not determined in the present study due to the frequency limit down to 100 mHz, $R_{\text{diffusion}}$ of the Li symmetric cell was clearly the smallest in the GBL-based electrolyte, which is six times smaller than the value in the DME-based electrolyte. As a result, the total resistances, including $R_{\text{diffusion}}$, can be smaller in the GBL-based electrolyte compared to that in the DMC- and DME-based electrolytes. Although battery performance can be affected by many factors such as the cut-off voltage, the distance between positive and negative electrodes (the thickness of separator), the loading level of the active materials (surface area and porosity of composite electrodes), and their balance in practical cells, this study demonstrated that the enhanced Li ion mass transfer in the GBL-based electrolyte associated with high $t_{\text{Li}^+}^{\text{current}}$ had a large impact on the discharge performance of the LCO cells at high current densities.

Conclusions

In this study, we evaluated the discharge rate capabilities of LCO half-cells using highly concentrated Li[FSA] with GBL-, AN-, DMC-, and DME-based electrolytes, and their relevance to the transport properties was studied. The PFG–NMR diffusivity measurements indicated that Li$^+$ ion diffusion was the fastest in the GBL-based electrolyte, whereas solvent diffusion was the fastest in the AN-, DMC-, and DME-based electrolytes. The fastest Li$^+$ diffusivity in the GBL-based electrolyte is considered to be due to the Li-ion hopping/exchange conduction in the chain-like Li-ion coordination
structure. We estimated the Li$^+$ transference number ($t_{\text{Li}^+}^{\text{current}}$) using the very-low-frequency impedance spectroscopy (VLF–IS) method. The minimum and maximum values of $t_{\text{Li}^+}^{\text{current}}$ (0.29 and 0.67, respectively) were obtained for the DME- and GBL-based electrolytes, respectively. For the discharge rate performances of the LCO half-cells, the GBL- and AN-based electrolytes exhibited high discharge capacities even at high current densities, while the DMC- and DME-based concentrated electrolytes showed severely decreased capacities at high current densities. The total overvoltage in the discharge profiles were discussed in terms of the resistances $R_{\text{ohm}}$, $R_{\text{interface}}$, and $R_{\text{diffusion}}$. As a result, $R_{\text{diffusion}}$ can be a critical parameter for determining the discharge performance at high current densities. The smaller $R_{\text{diffusion}}$ was found to result in higher discharge capacities in the GBL-based electrolyte. In this study, we demonstrated the importance of $t_{\text{Li}^+}^{\text{current}}$ on the rate capability of LCO cells with highly concentrated electrolytes for high-rate battery performance.

Conflicts of interest

There are no conflicts of interest to declare.

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Supplementary Information:

Viscosity ($\eta$), density ($d$), concentration of Li[FSA] ($c$), ionic conductivity ($\sigma$), and self-diffusion coefficients of electrolytes of the Li[FSA] concentrated electrolytes at 30 °C. Nyquist plots, and equivalent circuit (inset) for Li symmetrical cells by the very-low-frequency impedance spectroscopy (VLF–IS), galvanostatic discharge curves of Li/LiCoO$_2$ with different current densities, Nyquist plots, and equivalent circuit (inset) for Li/LiCoO$_2$ cells, the relationship between $R_{\text{ohm}}$ and the initial overvoltage, ohmic resistance ($R_{\text{ohm}}$), and interface resistance ($R_{\text{interface}}$) of Li/LiCoO$_2$.

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