

Article

A Liquid Inorganic Electrolyte Showing an Unusually High Lithium Ion Transference Number: A Concentrated Solution of LiAlCl_4 in Sulfur Dioxide

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Abstract: We report on studies of an inorganic electrolyte: LiAlCl_4 in liquid sulfur dioxide. Concentrated solutions show a very high conductivity when compared with typical electrolytes for lithium ion batteries that are based on organic solvents. Our investigations include conductivity measurements and measurements of transference numbers via nuclear magnetic resonance (NMR) and by a classical direct method, Hittorf's method. For the use of Hittorf's method, it is necessary to measure the concentration of the electrolyte in a selected cell compartment before and after electrochemical polarization very precisely. This task was finally performed by potentiometric titration after hydrolysis of the salt. The Haven ratio was determined to estimate the association behavior of this very concentrated electrolyte solution. The measured unusually high transference number of the lithium cation of the studied most concentrated solution, a molten solvate $\text{LiAlCl}_4 \times 1.6\text{SO}_2$, makes this electrolyte a promising alternative for lithium ion cells with high power ability.

Keywords: lithium ion transference number; lithium tetrachloroaluminate; sulfur dioxide; Hittorf's method; diffusion-ordered spectroscopy (DOSY)-NMR

1. Introduction

An electrolyte suitable for lithium ion batteries (LIBs) must fulfill several requirements to be useful for a secondary battery with high energy and power density as well as fast charging, safe operation and long lifetime [1–3]. Thermal, electrochemical and chemical stability and compatibility of all electrolyte components are basic requirements [4–6]. Furthermore, sufficient solubility of the salt and a high conductivity of the resulting electrolyte solution are required [4,5]. Other major requests include fast formation of a protecting solid electrolyte interphase (SEI) at the anode [7–9] and protection of the aluminum current collector from anodic dissolution [10,11]. Additionally, low costs of the electrolyte and non-toxicity matters for high volume production and consumer application. Currently, the most popular electrolyte for secondary lithium-ion batteries is based on LiPF_6 dissolved in a blend of linear and cyclic organic carbonate solvents like dimethyl carbonate (DMC) and ethylene carbonate (EC), respectively [12–14]. The salt LiPF_6 is a compromise but up to now it fulfills the often contradictory requirements mentioned above in the best way. Due to this situation, the search for better electrolytes for LIBs continues. Currently both, new salts with the commonly used organic solvents, e.g., lithium difluoro(oxalate)-borate in organic carbonates [15,16] as well as solutions of salts based on an inorganic solvent, e.g., LiAlCl_4 [4] or LiBr in SO_2 [17] are investigated.

The inorganic electrolyte LiAlCl_4 in liquid SO_2 shows at room temperature an extraordinarily high conductivity of about 70 mS cm^{-1} [18], by far outperforming a LiPF_6 /carbonate electrolyte (LiPF_6 in EC/DMC 1/1: 10 mS cm^{-1}) [19]. Another advantage is the non-flammability of this electrolyte when compared to LiPF_6 in organic solvents. A cell consisting of a LiCoO_2 -cathode, a lithium anode (plated on nickel substrate) and the inorganic electrolyte $\text{LiAlCl}_4/\text{SO}_2$ is chemically inert towards all cell components and has a cell voltage of 4 V [18,19]. Moreover, several intrinsic properties such as ion association, solvation and ionic transport are of great interest and explain some unusual properties [20,21]. The association constant of LiAlCl_4 in liquid sulfur dioxide are very small ranging from $42 \text{ dm}^3 \text{ mol}^{-1}$ at 238.15 K to $354 \text{ dm}^3 \text{ mol}^{-1}$ at 288.15 K despite rather low dielectric permittivity of the solvent [22–24]. These values reflecting ion-ion interaction have been determined by conductivity measurements and by evaluation of these data with the low-concentration chemical model established by Barthel *et al.* [23]. Compared to other salts (e.g., the association constant of LiBr in SO_2 is $96,100 \text{ dm}^3 \text{ mol}^{-1}$ at 298 K [24]), this small association constant entails also a high conductivity of concentrated solutions and a small loss of charge carrying lithium ions by ion pair formation. This property and the very high concentration of 6.2 mol L^{-1} of the salt in our transference number determination contribute to this unique fulfillment of some of the requirements as summarized above. The concentration of 6.2 mol L^{-1} is corresponding to that of a molten solvate of composition $\text{LiAlCl}_4 \times 1.6\text{SO}_2$.

The lithium ion transference number is another very important (but rarely determined) parameter for the characterization of lithium ion battery electrolytes. It represents the fraction of current carried

by lithium ions and it should be as high as possible. Zugmann *et al.* [4,25] have published a survey of various methods for determination of transference numbers based on various electrochemical methods, including the potentiostatic polarization method established by Bruce and Vincent [26], the galvanostatic polarization method according to Ma *et al.* [27], and the electromotive force method proposed by MacInnes and Beattie [28].

The potentiostatic polarization method is often used for solid polymer electrolytes or diluted electrolyte solutions [29]. Several conditions have to be met for this method, including ideal behavior of a binary electrolyte, reversible electrode reactions, and no convection. Compared with other methods, this method is less time-consuming and simple, but not useful for every electrolyte.

The galvanostatic polarization method is a very complex procedure to determine transference numbers. Parameters resulting from three independent measurements have to be combined for evaluating a single transference number, including cell potential after galvanostatic polarization, salt diffusion coefficient, and concentration dependence of the potential difference. This method is very time consuming, but it is suitable for non-ideal, concentrated solutions.

One of the first methods for determining transference numbers is the method established by Hittorf in 1853 [30]. With this method the quantity of migrated ions can be determined directly. The cell setup consists of a glass tube divided into at least three compartments and two electrodes for polarization with constant current. The transference number is obtained by determining the concentration difference evolved in the anodic and cathodic compartment. It has been determined in aqueous solutions by spectroscopic methods [31], conductometry [32–34], titration [35–38] and weighting [39,40].

Hittorf's method was applied by us to determine the transference number of this concentrated solution ($\text{LiAlCl}_4 \times 1.6\text{SO}_2$) as other methods cannot be applied for this electrolyte. The highly conductive electrolyte allows a realistic cell design, reversible lithium electrodes can be used and the determination of compartment's concentrations are very precise. Moisture sensitivity was utilized to fully hydrolyze the salt yielding four chloride ions from one tetrachloroaluminate ion. Subsequent concentration determination by potentiometric titration of the dissolved chloride ions with AgNO_3 is the method of choice used here. This method enhances the accuracy of the concentration determination by an amplification factor of at least four when compared to other methods, e.g., inductively coupled plasma-optical emission spectrometry (ICP-OES).

The transference number can also be determined by measuring the diffusion coefficient with nuclear magnetic resonance (NMR) spectroscopy if some precautions are taken into account [25,41,42]. This method is no electrochemical method and cannot distinguish free ions from ion pairs. In concentrated solutions this transference number can differ dramatically from transference numbers obtained by electrochemical methods and may even show erroneous concentration dependence [25].

As the association of this electrolyte (LiAlCl_4 in liquid SO_2) is rather small, the electrolyte was investigated with NMR-based diffusion measurements to determine the transference number and the Haven ratio $\Lambda_{\text{EC}}/\Lambda_{\text{NMR}}$, as well. This approach allows for an estimation of the association of ions based on the divergence of electrochemical and NMR-based ionic conductivities. The NMR-based diffusion measurement technique can also be applied for measuring transference numbers of and in ionic liquids [43,44].

2. Results and Discussion

The cationic transference number t^+ is the ratio of charge carried by Li^+ -ions and the total ionic charge passing the cell during the measurement time. The evolved concentration difference in the anodic and cathodic compartment is caused by electrode processes (plating and stripping of Li [45]) and by ion transport to sustain electroneutrality in the solution. If the chemical reaction is well known and no side reactions occur, the cationic transference number can be determined via the working equation according to Steel *et al.* [32]:

$$t^+ = 1 - \frac{|z| \cdot F \cdot \Delta c \cdot V}{Q} \quad (1)$$

where F is the Faraday constant; z is the formal charge; Δc is the difference between concentration of anodic compartment and electrolyte's initial concentration; V is the volume of the electrolyte in the anodic compartment; and Q is the charge passed via the cell during the measurement, respectively.

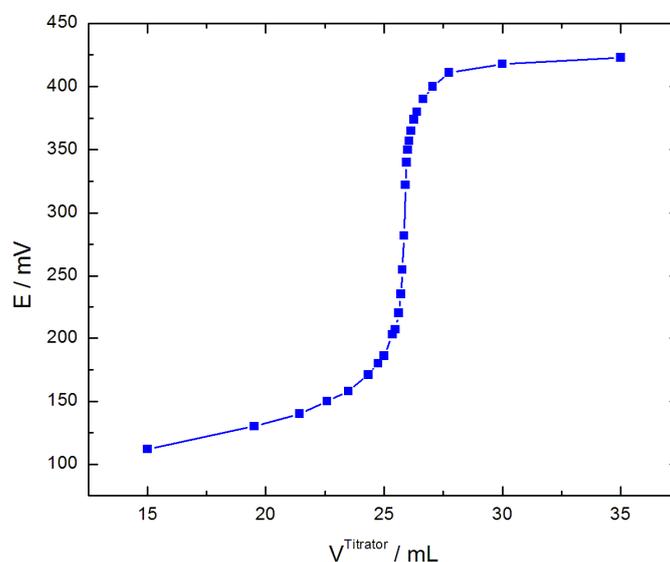
The concentration of the electrolyte c_{LiAlCl_4} was determined by potentiometric titration with AgNO_3 after full hydrolysis of the electrolyte (see Figure 1). Equations (2) and (3) result in Equation (4) which contains all measurable quantities, where $\rho_{\text{LiAlCl}_4 \cdot n \text{SO}_2}^{25^\circ\text{C}}$ is the density of the electrolyte; $m_{\text{LiAlCl}_4 \cdot n \text{SO}_2}$ is the mass of hydrolyzed electrolyte in anodic/middle compartment; n_{Cl^-} is the amount of chloride determined by potentiometric titration; m_{water} is the mass of water used for hydrolysis; and m_{tit} is the mass of titrand used for potentiometric titration:

$$c_{\text{LiAlCl}_4} = \frac{n_{\text{LiAlCl}_4}}{V} = n_{\text{LiAlCl}_4} \cdot \frac{\rho_{\text{LiAlCl}_4 \cdot n \text{SO}_2}^{25^\circ\text{C}}}{m_{\text{LiAlCl}_4 \cdot n \text{SO}_2}} \quad (2)$$

$$n_{\text{LiAlCl}_4} = \frac{n_{\text{Cl}^-}}{4} \cdot \frac{(m_{\text{LiAlCl}_4 \cdot n \text{SO}_2} + m_{\text{water}})}{m_{\text{tit}}} \quad (3)$$

$$c_{\text{LiAlCl}_4} = \frac{n_{\text{Cl}^-} \cdot \left(1 + \frac{m_{\text{water}}}{m_{\text{LiAlCl}_4 \cdot n \text{SO}_2}}\right)}{4 \cdot m_{\text{tit}}} \cdot \rho_{\text{LiAlCl}_4 \cdot n \text{SO}_2}^{25^\circ\text{C}} \quad (4)$$

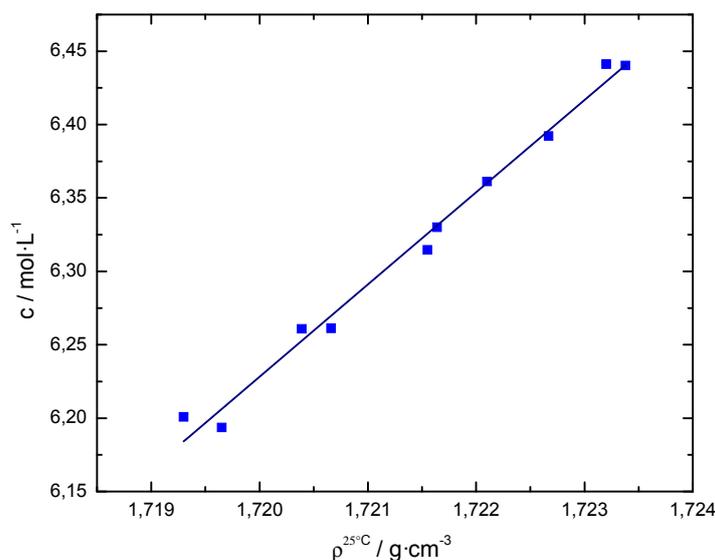
Figure 1. Typical titration graph, potential E vs. volume of the consumed silver salt solution.



This procedure results in an accuracy of concentration of about 0.01 mol L^{-1} a fact that is essential for reasonable transference number values.

Another very important parameter to obtain small error values is the very precise determination of density. The accuracy and repeatability of the density measurement was better than 0.0002 g cm^{-3} . In Figure 2, density data of several runs are correlated to the concentration of the electrolyte determined by potentiometric titration. This correlation allows linear fitting in the concentration range from 6.20 to 6.45 mol L^{-1} ($\sigma = 0.0096$).

Figure 2. Concentration vs. density of $\text{LiAlCl}_4 \times n\text{SO}_2$ in the concentration range 6.20 – 6.45 mol L^{-1} .



The results of Hittorf measurements are given in Table 1. During measurement the applied current was $I = 25 \text{ mA}$ and the temperature was $T = 298.10 \pm 0.05 \text{ K}$ and $298.30 \pm 0.05 \text{ K}$, respectively. V is the volume of the compartment/sample; Q is the total charge passing the cell during the experiment; and t^+ is the transference number referring to the initial concentration of the electrolyte. Despite several precautions, some convection and salt exchange from the anodic to the middle compartment could not be avoided completely. To correct this, the increase of concentration in the middle compartment was assigned to the quantity of the anodic compartment. This correction results in the transference number t_{corr}^+ .

Table 1. Results of Hittorf measurements.

Sample	V/mL	$\rho_{\text{LiAlCl}_4 \cdot n\text{SO}_2}^{25^\circ\text{C}} / \text{g cm}^{-3}$	$c_{\text{LiAlCl}_4} / \text{mol L}^{-1}$	Q/A s	t^+	t_{corr}^+
Electrolyte	3.3350	1.71965	6.194			
Anodic compartment	21.9024	1.72320	6.441	1665	0.69 ± 0.03	0.59 ± 0.07
Middle compartment	24.2503	1.72039	6.261			
Electrolyte	4.5914	1.71930	6.201			
Anodic compartment	21.3192	1.72338	6.440	1877	0.74 ± 0.03	0.59 ± 0.07
Middle compartment	23.3370	1.72164	6.330			

The uncertainty of the concentration c_{LiAlCl_4} [Equation (4)] was calculated by the appropriate error propagation law as follows:

$$\Delta c = \left| \frac{\partial c}{\partial n_{Cl^-}} \right| \cdot \Delta n_{Cl^-} + \left| \frac{\partial c}{\partial \rho} \right| \cdot \Delta \rho + \left| \frac{\partial c}{\partial m_{tit}} \right| \cdot \Delta m_{tit} + \left| \frac{\partial c}{\partial m_{water}} \right| \cdot \Delta m_{water} + \left| \frac{\partial c}{\partial m_{LiAlCl_4 \cdot n SO_2}} \right| \cdot \Delta m_{LiAlCl_4 \cdot n SO_2} \quad (5)$$

The estimated maximum errors are: Δn_{Cl^-} : 0.001 mmol (resulting from reading accuracy of the buret); $\Delta \rho$: 0.0002 g cm⁻³; Δm_{water} : 0.01 g and $\Delta m_{tit} = \Delta m_{LiAlCl_4 \cdot n SO_2} = 0.001$ g.

Taking into account all uncertainties, the cationic transference number t^+ of $LiAlCl_4 \times 1.6SO_2$ is 0.59 ± 0.07 . If the correction is not taken into account, the cationic transference number t^+ of $LiAlCl_4 \times 1.6SO_2$ would be 0.72 (average of two measurements resulting in 0.74 and 0.69).

Thus, we can emphasize here: the electrolyte $LiAlCl_4 \times 1.6SO_2$ offers in addition to the above mentioned properties an unusually high cationic transference number of about 0.6, which is nearly the double of that what has been observed in organic solvents.

In addition, the transference number was determined by diffusion-ordered spectroscopy (DOSY)-NMR experiments [46]. In infinitely diluted solutions, where no ion-ion-interaction occurs, the conductivity is correlated with the self diffusion coefficients via the Nernst-Einstein equation [Equation (6)] [47]. In concentrated solutions ion pair formation takes place and Equations (6) and (7) have to be employed with care, because the diffusion coefficients determined by NMR experiments do not distinguish between free ions, ion pairs and/or clusters. The theory claims free ions without any ion pair formation. Nevertheless, the degree of ion pair formation was estimated by the so-called Haven ratio H [Equation (8)], which is the ratio of electrochemical conductivity Λ_{EC} and the conductivity Λ_{NMR} [Equation (6)] calculated from diffusion coefficients obtained in concentrated solutions [47,48]:

$$\Lambda_{NMR} = \frac{|z| \cdot e \cdot F}{k_B \cdot T} \cdot (D^+ + D^-) \quad (6)$$

$$t_{NMR}^+ = \frac{D^+}{D^+ + D^-} \quad (7)$$

$$H = \frac{\Lambda_{EC}}{\Lambda_{NMR}} \quad (8)$$

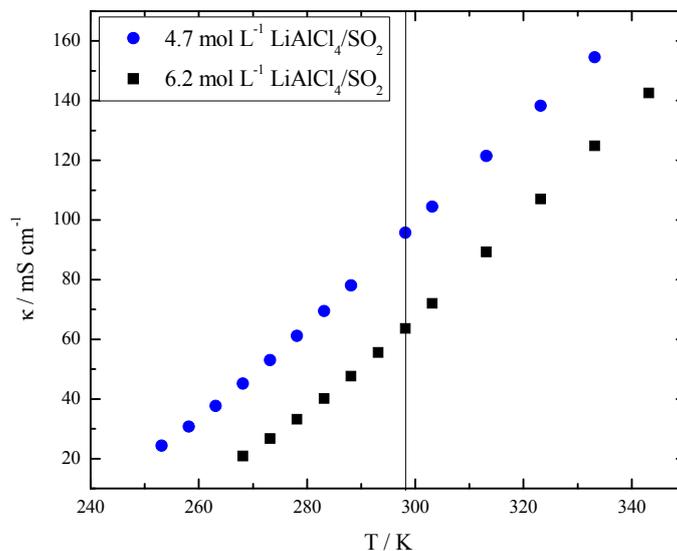
where $D^{+/-}$ is the diffusion coefficient of the anion/cation; k_B is the Boltzmann constant; z is the formal charge; e is the elementary charge; F is the Faraday constant; and T is the absolute temperature. The results of the conductivity measurements and DOSY-NMR experiments given in Table 2 include diffusion coefficients of lithium cations and aluminate anions, transference numbers of lithium cations t_{NMR}^+ , and the Haven ratio.

Table 2. Results of the conductivity measurements and DOSY-NMR experiments.

c/mol L ⁻¹	T/K	$\Lambda_{EC}/10^4$ S m ² mol ⁻¹	$D_{Li}/10^{-10}$ m ² s ⁻¹	$D_{Al}/10^{-10}$ m ² s ⁻¹	t_{NMR}^+	H
4.7	300	20.85	4.86	3.11	0.61	0.70
6.2	340	22.10	6.82	4.20	0.62	0.61

The temperature dependent specific conductivities of the 6.2 and 4.7 mol L⁻¹ are displayed in Figure 3.

Figure 3. Temperature dependent specific conductivity of 4.7 mol L⁻¹ and 6.2 mol L⁻¹ LiAlCl₄ in SO₂.

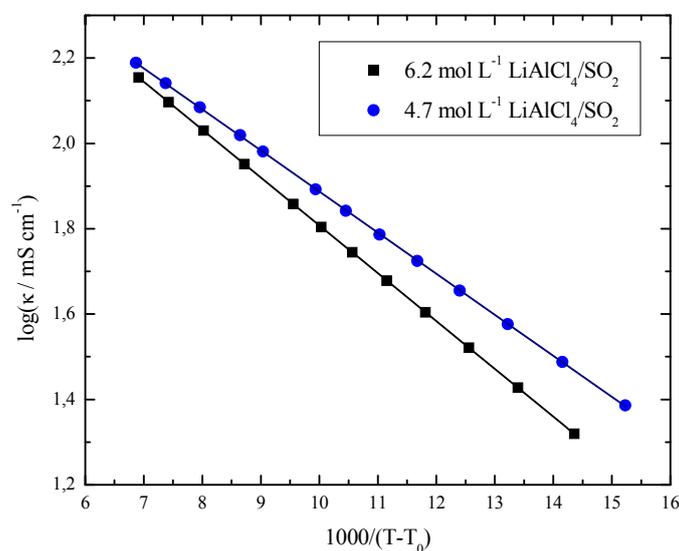


In 6.2 mol L⁻¹ solution, no ²⁷Al diffusion experiments could be performed for the anion at 300 K due to the fast quadrupolar relaxation of the ²⁷Al nucleus with T₁ and T₂ relaxation times of 6 ms. However, by increasing the temperature to 340 K and resulting deceleration of the quadrupolar relaxation, ²⁷Al diffusion experiment could be accomplished using the stimulated echo (STE) pulse program (less time-demanding DOSY experiments without eddy current delay).

Moreover, temperature dependent conductivities shown in Figure 3 follow a non-Arrhenius behavior (see Figure 4) and can be fitted by means of the empirical Vogel-Fulcher-Tammann (VFT) equation [Equation (9)] [49–52]. This is consistent with VFT-fits of concentrated electrolyte solutions of LiPF₆ in blends of organic solvents [e.g., EC and 2-methoxyethyl methyl carbonate (MOEMC)] [53]:

$$\kappa = \kappa_0 \cdot \exp\left(\frac{-B}{T-T_0}\right) \quad (9)$$

Figure 4. VFT-plot of the temperature dependent specific conductivities of 4.7 mol L⁻¹ and 6.2 mol L⁻¹ LiAlCl₄ in SO₂ and linear fitting.



In Equation (9), κ_0 is the specific conductivity at infinite temperature; B is a fitting parameter; and T_0 is the ideal glass transition temperature. The fitting parameter and their standard deviations are given in Table 3.

Table 3. VFT-fitting parameter of temperature dependent conductivities (also see Figure 3); σ is the standard error of the fitting parameters.

c/mol L ⁻¹	$[\kappa_0 \pm \sigma(\kappa_0)]/\text{mS cm}^{-1}$	$[B \pm \sigma(B)]/\text{K}$	$[T_0 \pm \sigma(T_0)]/\text{K}$
4.7	711.3 ± 10.2	222.1 ± 3.1	187.5 ± 0.7
6.2	849.9 ± 1.8	258.2 ± 0.5	198.5 ± 0.1

It is well known that ion-ion association is also temperature dependent and temperature dependence of conductivity results in change of concentration of free ions with temperature [4]. The very low association of the LiAlCl₄/SO₂ electrolyte, mentioned above, allows the assumption that the Walden rule can be applied. Commonly the Walden rule correlates the limiting molar conductivity Λ_m^0 with viscosity η and results in a constant term. But it was reported that concentrated electrolyte solutions (even ionic liquids) fulfill this correlation as well [52]. In rare cases where ion association is nearly negligible the same values are obtained for T_0 from both temperatures depended viscosity and conductivity measurements showing that the Walden rule dominates the behavior [54].

$B = D \times T_0$, where D is a parameter that describes the “strength” of a liquid according to Angell’s fragility concept [55]. The fragility m gives information about the temperature dependency of the liquid’s viscosity and is defined as the limiting slope in the plot of $\log(\eta)$ vs. T_g/T at the glass transition temperature T_g :

$$m = \left(\frac{d(\log(\eta))}{d\left(\frac{T_g}{T}\right)} \right) \text{ at } T = T_g \quad (10)$$

A higher fragility means a stronger change in viscosity near to the glass transition temperature.

Vilgis [56] developed a useful interpretation of the strength parameter D based on the average coordination number z_0 of molecules in the liquid state and its variability Δz :

$$D = \frac{1}{4} \cdot \left(\frac{z_0}{\Delta z} \right)^2 \quad (11)$$

Strong liquids with small m and large D show a small average coordination number of neighbored molecules in the liquid state. Network forming glasses such as SiO₂ or B₂O₃ are typical strong liquids with strong direct intermolecular interactions, having average values of z_0 around 3 to 5 [55]. They show a high resistance against structural change upon heating. *Vice versa*, weak liquids connected to a high fragility have weaker, non-directional intermolecular interactions with a much higher variability Δz in their average number of neighbors. They show high fluctuations in their non-organized dense packing and are much more susceptible for structural changes upon heating, *i.e.*, they show high fragility. If we accept applying Equation (9) for conductivities instead of viscosities for these solutions, we obtain an unusually low fragility parameter D of about 1.3 at 6.2 M and about 1.2 at 4.7 M, far below values reported up to date. This finding stresses again the weak and

easily re-orientating structures of the solutions considered here, a molten solvate with a deficit of solvent molecules even to fully solvate the cation alone.

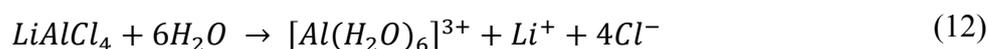
3. Experimental Section

First of all, it must be stressed that the studied electrolyte is extremely sensitive to moisture. Therefore, precautions were taken for every step of our experiments. This drawback comes along with a major advantage. It is immediately seen whether small traces of moisture have been present in the dried equipment. If so, a faint cloud appeared in the solution and the experiment was stopped. For additional information, see reference [22]. Furthermore, precautions have to be taken concerning the vapor pressure of the solutions: whereas the vapor pressure of liquid SO_2 is 0.276 MPa at 288.04 K and increases to 0.4608 MPa at 303.15 K [57], very concentrated solutions of LiAlCl_4 in sulfur dioxide show a significantly lower vapor pressure at room temperature (approximately 2 kPa) increasing to 0.1 MPa at 343.95 K [19].

The materials, $\text{LiAlCl}_4 \times n\text{SO}_2$ ($n \sim 1.5$) and the lithium bars were provided by Fortu Research GmbH (Karlsruhe, Germany) and used as received. For potentiometric titration, a standard solution of 0.1 N AgNO_3 (Carl Roth GmbH + Co. KG, Karlsruhe, Germany), Ag electrode (Ingold[®], Giessen, Germany), calomel reference-electrode (Metrohm[®], Filderstadt, Germany) and a salt bridge consisting of 4 M ammonium nitrate solution (salt from Merck[®], Darmstadt, Germany) are used. The water used for calibration of the densimeter and for hydrolysing the electrolyte was deionized by a Millipore[®]-equipment (Darmstadt, Germany). All weighting steps were done on a three-digit (Mettler[®] AT201, Columbus, OH, USA) or five-digit balance (Mettler[®] Toledo PB303-L, Columbus, OH, USA) considering the maximum balance weight.

The density of the electrolyte was determined by a flexural vibration DMA 60/602 from Anton Paar GmbH (Graz, Austria). The calibration was done according to manufacturer instruction with nitrogen and pure water (Millipore[®], Darmstadt, Germany).

The hydrolysis of about 5 g electrolyte with 50 g water was conducted in a round bottom flask (100 mL) by means of a dropping funnel. The setup was sealed by joint grease and clamps to avoid a loss of material. The hydrolysis was executed slowly and with great caution while stirring continuously. An alternating procedure of cooling with liquid nitrogen and warming by hands was applied to prevent a thermal runaway. The very exothermic hydrolysis reaction can be described as follows:



3.1. Potentiometric Titration

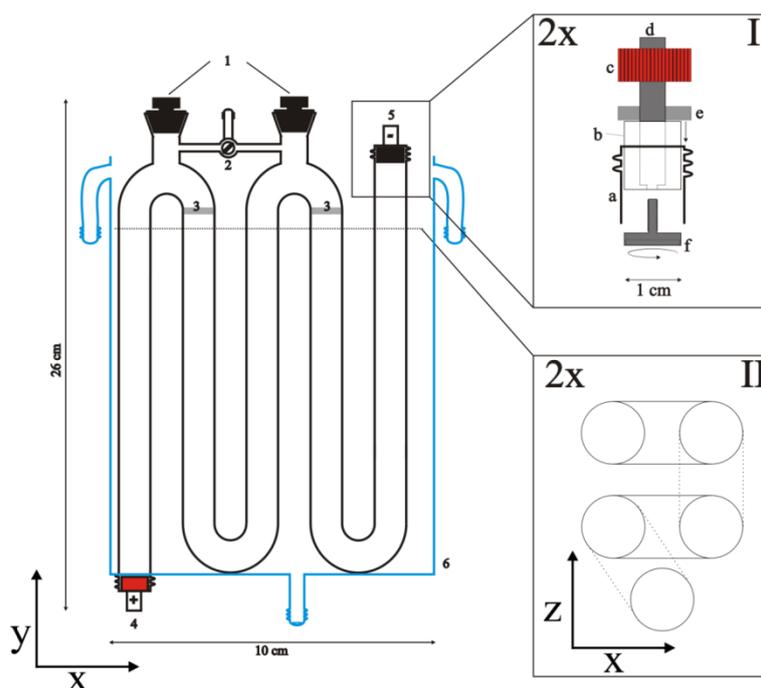
About 1.500 to 3.000 g of the hydrolyzed electrolyte was transferred into a flask filled with about 50 mL of 0.1 M HNO_3 . Afterwards the indirect determination of the electrolyte's concentration via potentiometric precipitation titration of chloride with AgNO_3 standard solution was performed. A 5 mL micro-buret (Brand[®], Munich, Germany) with an accuracy of ± 0.01 mL was used for titration and the potential was monitored by a multimeter (type: 196 System DMM;

Keithley Instruments Inc., Cleveland, OH, USA). The data processing was done with the software Maple 10 from Waterloo Maple Inc. (Waterloo, Canada); the data points were fitted with a spline function and the derivation of it was evaluated graphically.

3.2. Transference Number Measurements via Hittorf's Method

The transference number measurements were performed via Hittorf's method in the measurement cell shown in Figure 4. This cell was made in-house and takes account of good Hittorf cell design described in reference [30]. The cell consists of a folded tube made of Pyrex[®] glass (Schwerte, Germany) forming three compartments (anodic compartment, middle compartment and cathodic compartment). The compartments can be separated by extracting the electrolyte with a flexible Teflon tube and a syringe during nitrogen flow [Figure 4(5)]. Two glass frits are implemented to stop convection [Figure 4(3)]. The electrodes consist of stainless steel tips screwed through the Teflon bushing into a stainless steel cylinder [Figure 4(a–f)]. These tips were covered with lithium acting as electrodes.

Figure 4. Hittorf cell: 1: NS 14 ground glass joint; 2: three-way valve for inert gas flooding; 3: glass frit G 1; 4: anode; 5: cathode; 6: thermostat housing; a: glass tube; b: bushing (Teflon); c: screw cap; d: banana jack; e: O-ring sealing (Teflon); f: stainless steel electrode tip.



Moreover, the anode is at the bottom and the cathode at the top of the cell. This construction reduces the starting of convection because the density of the electrolyte increases nearby the anode caused by electrochemical oxidation of lithium and decreases at the cathode by reducing lithium ions. If the anode was at the top of the cell, the higher density of the electrolyte would induce severe convection. Finally, the temperature of the cell is controlled by a Julabo thermostat with an accuracy of 0.05 K.

The filling procedure was conducted in a glove box [Mecaplex, Grenchen, Switzerland; $\text{H}_2\text{O} < 0.5$ ppm, $\text{O}_2 < 5$ ppm, Argon 6.0 from Linde[®] (Munich, Germany)] with care to prevent bubbles. A lump of about 200 mg lithium metal was mounted on the special stainless steel anode and the cathode was covered by a piece of lithium stamped out from a stripe of lithium. Afterwards the ground joints were sealed with grease and the electrode-tips were fixed. Subsequently, the cell was tightened and assembled vertically outside the glove box to conduct the measurement. A current of 25 mA (32 mA cm^{-2}) was switched on for about 20 h to obtain the concentration difference which was used to determine the transference number of lithium ions. After polarization, the anodic and middle compartments were withdrawn by a flexible Teflon tube coupled to the tip of a syringe under nitrogen flow. The electrolyte of each single compartment was stored in a round bottom flask. Afterwards the electrolyte was hydrolyzed by a defined quantity of water. This procedure was carried out in a sealed apparatus, mentioned above. The concentrations in the cell's compartments (anodic and middle) and the initial concentration of the electrolyte were determined by potentiometric titration with AgNO_3 standard solution after hydrolysis as also mentioned above. Unfortunately the concentration in the cathodic compartment could not be determined because of bulky lithium growth.

3.3. Conductivity Measurement

The conductivity measurement was conducted using capillary conductivity cells [58,59], an in-house built symmetrical Wheatstone-bridge, with Wagner earth, resistance decade, and sine generator as described by Wachter *et al.* [60]. Cell calibration was done with a 0.1 mol L^{-1} solution of KCl in twice distilled water [61] obtaining cell constants of 38.41 cm^{-1} and 27.75 cm^{-1} . The cell filling procedure was executed in the glove box under argon atmosphere and closed gas-tight. Afterwards the conductivity cells were transferred to a thermostat assembly consisting of a cryostat (HM 90 EW, Holzwarth, Hof, Germany), power supply (EA-PS 3065-10 B, Elektro-Automatik GmbH & Co. KG, Viersen, Germany), proportional-integral-derivative (PID) controller, sinus generator, and resistance decade [62,63]. The electrolyte resistances were measured at frequencies of 1.7, 3.2, 5.1, 6.5, 7.7 and 10.1 kHz, respectively, and extrapolated to infinite frequency. With this setup a temperature stability of 2 mK [monitored by a ASL F-250 MkII thermometer (Automatic Systems Laboratories, Hampshire, UK)] and an accuracy of the calculated specific conductivity better than 0.1% was achieved.

The 4.7 mol L^{-1} $\text{LiAlCl}_4/\text{SO}_2$ solution was made by condensing dried sulfur dioxide in a flask loaded with the original electrolyte solution. Liquid sulfur dioxide (Linde 3.8) was stored in a gas-tight cold trap together with active basic aluminum oxide (Merck[®], activity stage I) > 12 h and subsequently condensed into the flask via stainless steel flexible tube. All involved equipment was dried at $60 \text{ }^\circ\text{C}$ in vacuum for more than 12 h; moreover, the ground joint fittings were sealed and dried by heat gun before connection to avoid recontamination with traces of water.

3.4. DOSY-NMR Measurements

The NMR measurements were performed inside a 5 mm pressure stable NMR tubes (Wilma 528-QPV-8, Griesheim, Germany) in 0.5 mL liquid SO_2 without field/frequency locking at 300–340 K. Tiny amounts (0.35–0.45 percent by weight) of tetramethylsilane (TMS) were added to each sample as

internal reference for the ^1H chemical shift and the diffusion coefficient of TMS was used to measure the viscosity of each sample. Referencing of the ^7Li and ^{27}Al chemical shift was done prior with reference samples of LiCl in D_2O and $\text{Al}(\text{iPr})_3$ in CDCl_3 , respectively. The spectra were recorded on a Bruker Avance III 400 MHz spectrometer (Bruker Biospin, Fallanden, Switzerland) equipped with a BBFO^{PLUS} room temperature probe with z-gradient (maximum gradient strength of 53.5 G cm^{-1}) and BVT 3200 temperature control unit.

The diffusion measurements were performed with standard Bruker STE for ^{27}Al and longitudinal eddy current delay with bipolar gradient pulses (BPLED) for ^1H and ^7Li sequences in a pseudo 2D mode. For each experiment, two dummy scans and minimum sixteen scans were used with a relaxation delay of 1–2 s. The length of the gradient pulse δ was optimized for every nucleus in each sample and a diffusion time Δt of 35 ms for ^{27}Al and 50 ms for ^1H and ^7Li was used for all experiments. Sinusoidal shapes were used for the gradients and a linear gradient ramp with minimum twelve increments between 5% and 95% of the maximum gradient strength was applied for the diffusion relevant gradients. For the homospoil gradients, 9.165 and 7.046 G cm^{-1} were applied for HS1 and HS2. The spectra were processed with the Bruker program Topspin[®] and the diffusion coefficients were calculated with the Bruker software T1/T2 package.

4. Conclusions

The cationic transference number of $\text{LiAlCl}_4 \times 1.6\text{SO}_2$ was determined by a classical Hittorf measurement and also calculated from diffusion coefficients that were determined via DOSY-NMR. Moreover, the Haven ratio $\frac{A_{EC}}{A_{NMR}}$ was calculated to estimate the association behavior of this very concentrated electrolyte solution. Additionally, the temperature dependent specific conductivity of 4.7 mol L^{-1} and 6.2 mol L^{-1} LiAlCl_4 dissolved in SO_2 was measured in the temperature range from 260 K to 340 K. A linear correlation of density and concentration was obtained in the concentration range from 6.20 to 6.45 mol L^{-1} . The very high transference number of this electrolyte and the very low tendency to association decreases the concentration polarization in LIBs. The solutions also show unusually low fragility parameters of about 1.3 at 6.2 M and about 1.2 at 4.7 M, far below values reported up to date. This finding stresses again the weak and easily re-orientating structures of the solutions considered here, a molten solvate with a deficit of solvent molecules even to fully solvate the cation alone. The electrolyte $\text{LiAlCl}_4 \times 1.6\text{SO}_2$ offers in addition to several known properties an unusually high cationic transference number of about 0.6, which is nearly the double of that what has been observed in solutions with organic solvents. Therefore, this electrolyte is a promising alternative for high power secondary lithium ion batteries.

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Conflicts of Interest

The authors declare no conflict of interest.

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