Transport properties of lithium-ion in green nonaqueous solutions and polymer ionic exchange membranes: an attempt to elaboration of ecological Li-ion battery

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Abstract

Organic solutions are considered as good electrolytes yielding higher lithium-ion (Li-ion or Li^+) transference numbers for lithium-ion batteries during charge and discharge processes. However, owing to ecological reasons, the transference numbers of this metal ion in green viscous solvent such as glycerol at various concentrations and temperatures have been measured by means of the concentration cell and Bruce–Vincent techniques. An average value of the transport number less than 0.5 was obtained at 298.15 K, suggesting that the solvated Li^+ carries less electric charges than the larger size chloride anion. The results were then compared to a recent study utilizing molecular dynamics simulation where it was confirmed the smallness values of the Li^+ transference number. Besides, Hittorf's method using the polymer cation exchange membrane (nafion 117) has been also investigated and shows the highest transport, suggesting its advantageous utilization in ecological lithium-ion batteries. Furthermore, the concentration polarization of membrane equilibrated with the electrolyte solution of lithium was carried out by means of voltamperometry that allowed recording the current–voltage characteristic. It yielded, however, low limiting current density, indicating that the polarization is more pronounced with such light metal, in contrast to larger diffusion constant and average transport number.

Keywords Nonaqueous electrolyte · Polymer exchange membrane · Electrochemical methods · Transport · Li-ion

1 Introduction

Owing to its high energy density, Li-ion is widely used in the elaboration of electric power devices, in particular lithium-ion batteries [1]. These latter are extensively utilized in various portable electronic devices (i.e., mobile phones, electronic tables, etc.)... [2, 3]. At very small scale, Li-ion batteries can be used for high-temperature sensing applications [4]. They also present potential applications toward energy sustainability and consequently substantial carbon emission reduction [5]. Moreover, due to its high reactivity

with oxygen, the electrolytes commonly used in such devices are mixtures of organic solvents and lithium-based salts. Recent experimental study on the electrical conductivity of solutions of lithium bis(fluorosulfonyl) imide (LiFSI) in organic solvents: dimethyl carbonate (DMC), ethylene carbonate (EC) and propylene carbonate (PC), was carried out for low concentrations at ambient, pressure and temperatures between 293 and 333 K, for solvent optimization in lithium-ion battery [6]. More recently, valeronitrile has been proved to be a good solvent for the salt lithium bis(fluorosulfonyl) imide (LiFSI) in lithium batteries, since it

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forms complexes with the Li^+ -ions. The complexation was studied by various spectroscopies such as optical, Raman, infrared and nuclear magnetic resonance. Based on the spectroscopic information, a chemical model for the complexation was developed and the equilibrium constants for the formation of the different species were obtained [7].

Moreover, as reported by Izustu [8], the lithium secondary batteries can use either solid and gel polymer electrolyte that dissolve lithium salt. However, their electrical ionic conductivities are lower and their applications are limited to batteries of low current densities. Nevertheless, enhanced ionic conductivity and interface stability of hybrid solid-state polymer electrolyte for rechargeable lithium metal batteries have been described elsewhere [9]. While, in gel polymer electrolytes, conventional electrolyte solutions may be used, but their splitting from the batteries can be avoided by gel formation with polymers [8].

Furthermore, in order to avoid pollution and preserve the environment, nowadays, considerable research is being undertaken in this new topic by using ecological friendly solvents such as glycerol. Glycerol is a cheap, colorless, odorless, viscous and nontoxic organic low molecular weight component endowed with glass transition and melting process features [10]. Besides, it exhibits a number of features such as glass-forming behavior, low glass transition temperature, high flexibility of the backbone and efficient coordination of lithium-ions that make it an appealing ion-conducting medium and a challenging building block in the preparation of new inorganic–organic polymer electrolytes [11]. On this basis, the study of the physicochemical properties and the charge migration mechanism of polymer electrolytes high viscous glycerol carrying lithium-ions become interesting in the development of next-generation lithium batteries. Recently, Pagot et al. studied some glass-forming electrolytes that are based on lithium glycerolate, to be utilized as potential electrolytes in Li-ion batteries [12].

Due to its importance, Li^+ transport and the true transference number in nonaqueous polyelectrolyte solutions for Li-ion batteries have been recently investigated and are studied using all-atom molecular dynamic simulations [13]. An optimal composition was therefore sought: maximizing electrical conductivity and minimizing conductive salt content. Improving the transference number of Li^+ electrolytes is an important area of research to improve the energy density and charge rates of Li-ion batteries. There are systems that could lead to high transference number, high conductivity solid electrolytes such as lithium ceramics, nonflammable perfluoropolyether, binary salts and solvent-filled ionomer membranes, as well as liquid electrolyte solutions (i.e., salt-tethered nanoparticles dispersed in liquid solvents, solvent-in-salt and polyelectrolytes [14].

The transport of Li^+ in such electrolytes seems to be a problem when the battery produces higher current densities, thus reducing its performance. The study of long life Li-ion battery with enhanced electrode/electrolyte interface by using ionic liquid solutions has been widely reported [15]. It is therefore interesting to investigate the transport properties of the electrolyte in particular its electric conductivity and the transport number of the Li^+ [16]. In an electrolyte solution, the electric current is transported both by the cation and the anion, where the transport number (TN) of the Li^+ is supposed to be higher. However, a large transport number can reduce inconveniently the concentration gradient during the charge–discharge steps of the battery. Nevertheless, it is not always the case; many available electrolytes display transport numbers less than 0.5 [17, 18].

Barthel et al. [19] reported in the literature that transference numbers of cations at infinite dilution less than 0.5 decrease with increasing concentration and decreasing temperature, while those greater than 0.5 vary in the opposite way. The possibility of reversing the sign of temperature and concentration dependence by the choice of an appropriate electrolyte can be utilized in elaboration of batteries. This is very probably recommended when electrolytes with high mobility of the active ion at low temperature are sought in technological applications requiring specific charge transport properties.

On the basis of all these interesting studies and following our previous investigations on measurements of conductivity lithium chloride in glycerol [20, 21], the present study involves the measurement of the TN of the Li^+ in such highly viscous organic solvent, with view perhaps to use the electrolyte in an ecological green friendly battery. Three methods were therefore utilized which are namely concentration cells [22–24], Bruce–Vincent technique [25–27] and Hittorf's method using polymer exchange membrane [28, 29]. In this latter, the electrolyte acts a separator and ionic conductor between cathode and anode, generally a solid ion-conducting membrane. It is required to electronically separate the two electrodes, and at the same time, it must be porous and allow the ions to flow through it. Moreover, polymer gel electrolytes are common types of membranes used in lithium-ion batteries. They prevent the positive and negative electrodes electrically contacting each other and allow rapid ionic transport to complete the circuit for the passage of current in Li-ion batteries, by increasing their energy efficiency [30].

However, in contrast to bulk solutions, the current within the membrane is almost exclusively carried by the counter-ions. As a result, concentration gradients can be formed in the boundary layers adjacent to the membranes [31, 32]. On the dilute side, the concentration decreases with respect to the bulk concentration,

whereas it increases on the concentrate side of the membrane. When the current increases, the counter-ion concentration nearby the membrane surface, on the dilute side, decreases. At an optimum current density, the concentration vanishes and as a result, a limiting current density is reached. The concentration polarization may produce problems at elevated current density and therefore an increase in electrical energy consumption in the membrane process (i.e., electrodialysis) [33]. The concentration polarization in ionic exchange membrane has been already explained for the first time by carrying out measurement of current–voltage curves by Spiegler [31] and later on explained theoretically by Aguilera [34]. In 2004, Tannaka [35] showed that concentration polarization occurs more easily on the cation exchange membrane than on the anion-exchange membrane. In order to understand the limiting current, the type, the concentration, the mass and the valence of charge carriers across the membranes have to be identified [36]. Therefore, an investigation with current–voltage has been carried out using the Nafion membrane which may be used as a separator in a Li-ion battery.

Furthermore, the TN data obtained with the concentration cell method were fitted to empirical power law [37] and Vogel-Tamman-Fulcher equation [38], in the temperature range (0–30 °C) and discussed in relation to the ion transport phenomena taking place in the viscous hydrogen-bonded solvents.

2 Methods

Transference number is an important parameter to describe the transport of ionic species in electrolyte solutions. There are three methods used to determine this number, which are liquid junction concentration cell, Bruce–Vincent method and Hittorf's method.

2.1 Liquid junction concentration cell

Following previous investigation showing the reliability and accuracy of concentration method in nonaqueous solution, we carried out experiments at reduced temperature down to 0° C with glycerol with the aim perhaps to study its behavior in future in the super-cooled liquid state (down to – 100 °C). When two electrolyte solutions of different concentrations and the same solvent contact each other at a junction, ion transfers occur across the junction. If the transfer rate of the cation differs from that of the anion, a charge separation occurs at the junction and potential difference is generated. The potential difference tends to retard the ion of higher rate and accelerate the ion of lower rate. Eventually, the rate of both ions is

balanced and the potential difference reaches a constant value. This potential difference is called the liquid junction potential (E_{LJ}) [24].

The electromotive force with liquid junction (E_{LJ}) may be generated in an electrochemical cell composed of two half-cells having the same electrolyte and different concentrations (i.e., $C_1 = x.C_2$). The half-cells are linked by liquid junction. The value of the E_{LJ} measured by means of two reversible electrodes to anion may be given by Nernst equation (Eq. 1) [24].

$$|E_{LJ}| = + \frac{2RT}{F} \int_1^2 t_+ d \ln a_{\pm} \quad (1)$$

where t_+ is the TN of cation, ($a_{\pm} = \gamma_{\pm}C$) the mean ionic activity of electrolyte, R the gas constant, F the Faraday constant and T the temperature. But, if we assume the transference number constant within the concentration range of the cell, (Eq. 1) becomes

$$|E_{LJ}| = \frac{2RTt_+}{F} \ln \left(\frac{\gamma_1 C_1}{\gamma_2 C_2} \right) \quad (2)$$

So, for each concentration range, (Eq. 2) has been used to deduce the transference number from the measured E_{LJ} and the calculated values of γ_1 and γ_2 using Debye–Huckel limiting law (Eq. 3) [24].

$$t_+ = \frac{E_{LJ}F}{2RT \ln \frac{\gamma_{\pm 1} C_1}{\gamma_{\pm 2} C_2}} \quad (3)$$

with:

$$\ln_{\pm} = - \frac{e^3 (2N_0 C)^{\frac{1}{2}}}{8\pi(\epsilon_0 \epsilon_r K T)^{\frac{3}{2}}} \quad (4)$$

2.2 Bruce–Vincent method

This method can also be used to determine the transference number of ionic species in polyethylene electrolytes. It has already been tested in the study of ion transport and thermal properties of poly(ethylene oxide)—lithium perchlorate polymer electrolytes [39]. It is therefore convenient to high viscous electrolytes solutions such as glycerol. It is based on a combination of direct current (D.C.) polarization and alternating current (A.C.) analysis. Basically, the method consists of measuring by D.C. chronoamperometry and A.C. impedance, respectively, the current across a symmetrical electrolyte solution and an A.C. resistance inside an electrochemical cell, polarized by a D.C. pulse

voltage. The transference number of the cation t_+ may be determined by using the following expression [26]:

$$t_+ = \frac{I_s(V - I_0 R_0)}{I_0(V - I_s R_s)} \quad (5)$$

where V is the value of the D.C. pulse voltage applied to the cell, R_0 initial resistance of the cell, R_s the resistance at steady state, I_0 and I_s initial and steady-state currents, respectively.

2.3 Hittorf's method

This method is suitable to determine transference numbers of ionic species through solid electrolytes such as polymer ionic exchange membranes. An estimation of Li^+ TN in polymer electrolytes by the combination of complex impedance and potentiostatic polarization measurements have already been undertaken [40]. The permselectivity of MEI, i.e., their ability to ensure the transport of the counter-ions (ions associated with the fixed sites of the membrane) while being impermeable to co-ions is characterized for a given ion by the TN. This latter is defined as the fraction of the current carried by this ion. In a perfectly selective membrane, the TN of the counter-ions is equal to the unit while that of the co-ions is zero. In all cases, the sum of the TNs is equal to unity. The TN can be calculated using Eqs. 6 or 7:

$$t_+ = \frac{z_+ J_+ F}{j} \quad (6)$$

where z_+ is the valence of the ion, J_+ its flux ($\text{mmol cm}^{-2} \text{ s}^{-1}$), F Faraday constant and j the current density (A cm^{-2}) [27, 28]. Equation 6 may be re-written as

$$t_+ = \frac{z_+ C + VF}{It} \quad (7)$$

where C_+ is the concentration of lithium transferred through the membrane (mmol L^{-1}), V the volume of the cathode compartment, I the current applied (A) and t the duration of the experiment.

3 Experimental

3.1 Electrochemical cells used for determination of Li^+ transference numbers

Three methods were used to determine the TN of lithium-cation, which are namely: concentration cells

Fig. 1 Schemes of electrochemical cells used for determination of lithium TNs using: **a** concentration cell, **b** Bruce–Vincent method and **c** Hittorf's method

(Fig. 1a), Bruce–Vincent method (Fig. 1b) and Hittorf's method (Fig. 1c).

3.1.1 Design of concentration cell with liquid junction and procedure

The cell used for measurements with transference consisted of U-tube with stopcock. This latter permitted separation of the solution in the two limbs 5 cm in height and 0.5 cm in diameter. When the two solutions were at the same level in the two limbs of the U-tube, junction between them was made by opening the stopcock. With this cell design, we had less diffusion problem with glycerol than water.

The U-tube was filled with solution and put inside a double envelope Pyrex cell which was connected to a cryostat filled of ethylene glycol by means of a plastic pipe, where the temperature was maintained constant to a desired value. Next, the silver/silver chloride (Ag/AgCl) electrodes were placed in the two limbs and the whole allowed equilibrium for 15 min. When the junction was made, the voltage was taken after 20 min using a digital voltmeter. Owing to their different diffusions, the voltage was steady within 0.5 mV.

The whole experimental setup for temperature control consisted of the cryostat (Lauda) which was linked to the big double envelope glass cell by plastic tubes. The small measuring Pyrex cell was inserted into the big cell to allow the temperature to be reached during 1 h before measurements. The temperature was checked by means of an electronic thermometer placed inside.

3.1.2 Design of Bruce and Vincent cell and procedure

On the basis of Bruce and Vincent method, we have used a 40 mL Pyrex vessel in which two Ag/AgCl plates were dipped at a fixed position, 2 cm apart. When the solution was poured into the vessel, the direct current voltage pulse of 20 mV was applied for 15 min to the cell to allow polarization. Then, the feed current was switched off and the voltage of the cell was followed during 20 min, which was steady within 2 mV. Therefore, the initial and final values of the voltage were recorded. Besides, the values of the initial and final resistances were measured by alternating current to deduce initial and final currents. Moreover, for the temperature control, the same method was followed as before.

3.1.3 Design of Hittorf's cell

In this method, symmetrical two-compartment glass cell was used. The anodic compartment contained 50 mL of Li^+ -glycerol (100 mmol L^{-1}) and the cathodic compartment contained 50 mL of potassium electrolyte (100 mmol L^{-1}). The compartments were separated by the cation exchange membrane Nafion 117. The galvanostatic mode allowed an average current of 31.4 mA under the applied voltage 5 V between two stainless steel electrodes during 30 min. The working area of the membrane was 3 cm^2 . Magnetic stirrers ensured homogeneity of the solutions. During the electrolysis, the ions in solution move freely, but the situation is quite different through the membrane. In effect, the lithium cations (Li^+) of opposite charge (counter-ions) to the functional sulfonic groups (i.e., SO_3^-) of the membrane

were exchanged normally and moved from the anode compartment toward the cathode compartment, while those of the same charge (co-ions) were automatically repelled by electrostatic effect.

3.1.4 Voltamperometry set up

Current–voltage characteristics were obtained using the voltamperometry set up represented by Fig. 2. It is made of Plexiglas and consists of two symmetrical compartments (70 mL). The feed electrodes consist of titanium sheets coated with platinum. The effective area of the membrane was 5 cm^2 . In addition to the feed platinized-titanium electrodes, two silver–silver chloride electrodes were placed nearby the membrane sides, for measurement of the transmembrane potential difference for each value of the applied current. In order to control both the current intensity and the voltage, two digital meters were placed, respectively, in series and in parallel to the cell.

4 Results and discussion

4.1 Electrolyte solution data

The performance of conventional Li-ion battery is limited by its low transference number of the cation, defined as the fraction of ionic conductivity imparted by Li^+ rather than its counter-ion. The low cation transference number generally less than 0.5 corresponds to the electrolyte in which the anion is highly mobile, whereas the electrochemically active Li^+ moves more sluggishly as a result of its bulky solvation shell. In consequence, the concentration

Fig. 2 Schematic diagram of a two-compartment electrolytic cell used for current–voltage measurements

gradient forms in the electrolyte, which limits the material utilization, promotes the lithium plating and generates the concentration overpotentials, all of which contribute to lowering the power density, and thus reducing the cell's lifetime [13].

4.1.1 TN from concentration cell

The TNs of Li^+ were determined by the three different electrochemical techniques, namely concentration cell, Bruve-Vincent method and Hittorf's method using ionic exchange membrane. As reported in the literature, for the concentration of cell technique, the TN can be obtained from the ratio between the EMF of the concentration with transport (i.e., with liquid junction) and the EMF of the concentration without transport (i.e., with amalgam link) [23, 24, 41]. This method works correctly with alkali and alkaline-earth metals such as potassium, sodium and nickel. However, it does not seem to be reliable with the very reactive Li-ion; the amalgam concentration cell yields unfortunately erroneous data. Thence, only the liquid junction concentration was used for further measurements.

Hence, for the concentration of cell 100/50 (mmol L^{-1}) Eqs. 3 and 4 were combined to give the TN 0.395 at the temperature of 25 °C. This value compares well with those obtained by Champeney et al. [23] for solutions of potassium chloride and sodium chloride in glycerol at a concentration of 100 mmol L^{-1} (i.e., 0.479 and 0.417). Indeed, it follows logically the reasonable order $t_{\text{Li}^+} < t_{\text{Na}^+} < t_{\text{K}^+}$, which is in good correlation with the standard Gibbs energies of these cations, i.e., $\Delta G_{\text{hyd}}^0(\text{Li}^+) > \Delta G_{\text{hyd}}^0(\text{Na}^+) > \Delta G_{\text{hyd}}^0(\text{K}^+)$, as well as their enthalpies of hydration $\Delta H_{\text{hyd}}^0(\text{Li}^+) > \Delta H_{\text{hyd}}^0(\text{Na}^+) > \Delta H_{\text{hyd}}^0(\text{K}^+)$ [8].

4.1.2 TN versus concentration

Figure 3A shows that the TN of Li^+ increases with increasing concentration. This variation is reasonable and fulfills the requirements of those metal ions having TNs less than 0.5 at infinite dilution. This finding is in quite qualitative accordance with the results presented in Fig. 3B that were calculated for the true transference data obtained from ionic conductivity using nonaqueous polyelectrolyte solutions data [13]. The true transference number (t_{Li^+}) calculated from ionic conductivity data is plotted along with the TN using molecular dynamics simulation with values for the charge of the anionic species (z_-) of both -1 and $z_{\text{polymer}} = -43$. For instance, at concentration 1 M, they yielded TNs equal almost to 1.0 and 0.5, respectively, and suggested that singly charge anions allowing higher values of the transport number. Furthermore, we demonstrate and confirm in our present investigation that the negatively charged chloride ion is becoming much larger

Fig. 3 **A** Variation of transference of lithium-ion with concentration at 298.15 K. **B** True transference number (t_+) calculated from ionic conductivity data is plotted along with the transport number (t_{NMR} , an approximation of t_+ for ideal systems). Values for the charge of the anionic species (z_-) of both -1 and $z_{\text{polymer}} = -43$ are used in calculating the transport number [Ref. 13, p. 1255]

in size and carrying much electric current. It is therefore responsible for the majority of the solution conductivity at all concentrations, corresponding to Li^+ transference numbers much lower.

In effect, the structural and transport properties of a nonaqueous polyelectrolyte solution was recently

Table 1 Transport numbers (TN) of lithium in glycerol $C = 100 \text{ mmol L}^{-1}$ using Bruce–Vincent method at 25°C

Frequency, f (Hz)	Initial current, I_0 (mA)	Steady current, I_s (mA)	Initial resistance, R_0 (k Ω)	Steady resistance, R_s (k Ω)	TN, t_{Li^+}
100	167 ± 2	183 ± 2	173	304	0.569 ± 0.005
200	223 ± 3	265 ± 3	130	211	0.616 ± 0.004
1000	138 ± 2	145 ± 2	209	385	0.543 ± 0.005
5000	280 ± 3	290 ± 4	104	187	0.556 ± 0.003
20,000	166 ± 2	189 ± 2	174	296	0.588 ± 0.005

investigated using molecular dynamics simulations, where it has been proved that after deconvoluting the total ionic conductivity into contributions from each type of correlated and uncorrelated ion motion, it has demonstrated the substantial impact of cation–anion and anion–anion correlations. These non-ideal ion correlations substantially decrease the cation transference number. The ion transport mechanisms will thus inform the design of improved polyelectrolyte systems for Li-ion batteries and generally enhance understanding of charge transport in polyelectrolyte solutions [13].

4.1.3 TN from Bruce–Vincent method

This method was based on the application of a D.C. voltage, and values of initial and steady currents I_0 and I_s were deduced. These currents required values of initial and steady resistances of the cell, which were measured under the application of A.C. at higher frequencies to minimize effect of capacitance of double layer. By spanning the frequency range $[10^2 - 2 \times 10^4 \text{ Hz}]$, the TN of Li^+ changes slightly reaching its mean value laying between 0.543 and 0.588. The values at different frequencies are given in Table 1. If one considers the experimental uncertainty, one can assume the value of the TN equal to 0.543 corresponding to the nominal frequency 1000 Hz. Though the method is completely different from that of the concentration cell, it gives fortunately that TN which is not far away from that found with the concentration cell $100/50 \text{ mmol L}^{-1}$ at 25°C (i.e., 0.381). The difference between the two sets of data may be due to the methods used throughout.

4.1.4 Effect of temperature on TN

As shown in Fig. 4, the EMF of the concentration cell with liquid junction increases with the temperature, as the chemical reaction of oxidation and reduction involved at electrodes become more pronounced. The TNs of Li-ion (t_{Li^+}) in glycerol were determined at various temperatures and concentrations. They were obtained from EMF measurements using Nernst equation and Debye–Huckel limiting law of mean ionic activity. The data of the

Fig. 4 Evolution of electro-motive-force (EMF) of concentration cell $100/50 \text{ mmol L}^{-1}$ **Table 2** Values of EMFs, activity coefficients (AC) and transport numbers (TN) of lithium in glycerol at different temperatures using the concentration cell (CC) $100/50 \text{ (mmol L}^{-1})$

Temperature (K)	EMF (mV)	γ_1	γ_2	t_{Li^+}
273.15	1.62 ± 0.05	0.346	0.472	0.089 ± 0.003
278.15	2.50 ± 0.10	0.357	0.482	0.134 ± 0.003
283.15	3.50 ± 0.15	0.366	0.491	0.189 ± 0.005
288.15	5.38 ± 0.20	0.376	0.501	0.289 ± 0.008
293.15	7.34 ± 0.35	0.385	0.509	0.356 ± 0.011
298.15	8.30 ± 0.45	0.398	0.521	0.381 ± 0.020
303.15	9.84 ± 0.50	0.404	0.527	0.434 ± 0.022

concentration cells $100/50$ are given in Table 2. It can be seen from Fig. 5 that, as expected, t_{Li^+} increases with an increase in temperature, making in evidence that the greater activation energy of the cation Li^+ than that of the anion Cl^- , as has been already pointed out by Munchi et al. with measurements of lithium TNs in polyethylene oxide complexes [42]. On the other side, the trend of our temperature curve is similar to that found in previous data of aqueous solution [43]. Glycerol is similar to water in that it is a hydrogen-bonded solvent, it has three hydroxyl groups, and it has a relatively higher

Fig. 5 Dependence of transport number (TN) of lithium-ion upon temperature using concentration cells 100/50 and 500/50 mmol L⁻¹: effect of concentration gradient

dielectric constant ($\epsilon_r = 42$). Besides, the dependence of the transference number on the temperature decreases as the concentration gradient is increased. When the temperature changes the TN of Li⁺ behaves in the same manner either in liquid or solid electrolytes. The data of the concentration cell 100/50 mmol L⁻¹ were further analyzed by fitting them to power law and Vogel–Tamman–Fulcher empirical equation [37, 38].

4.1.5 Fitting procedure to power law and VTF equation

Owing to its potential applications in high viscous solvents [37] and polymer-based electrolytes [44], the TN data of Li⁺ were fitted to the power law and Vogel–Tamman–Fulcher (VTF) equation using Eqs. 8 and 9. The fittings were carried out as follows. An arbitrary value of the fitting parameter (n) was fixed, and least square analysis was performed, to yield the best values of the fitting parameters A' and B' . Following a previous study on conductivity of KCl in glycerol [37], the values of (n) were scanned from 3 to 4 in steps of 0.1, and residual sum of squares showed a minimum at about 3.11. While with the VTF equation, the least square analysis gave the values of other fitting parameters C' , D' and T_0 (an arbitrary chosen temperature usually less than glass transition temperature of super-cooled liquids [37]). The same procedure was followed with the data of the activity coefficient (γ_1). The values of all these parameters along with those taken from literature [37, 42] are summarized in Table 3. Plots of $\ln(\text{TN})$ versus $(10^3/T)^{3.11}$ and $\ln(\text{TN})$ versus $10^3/(T-117)$ are given in Figs. 6 and 7 where the straight lines correspond to the fitted equations with linear regression coefficients (R^2).

Approximately, the same trends were obtained with the activity data with similar values of n and T_0 (Figs. 8, 9).

Table 3 Fitting parameters using power law and Vogel–Tamman–Fulcher equation

Solution	Parameter	Power law	VTF equation	Temperature range (K)
Glycerol + LiCl (our data)	Transport number (TN) using CC 100/50 mmol L ⁻¹	$n = 3.11$	$T_0 = 117 \text{ K}$	273.15–293.15
		$A' = +4.785$	$C' = +10.09$	
		$B' = -0.127$	$D' = -1.951$	
Glycerol + LiCl (our data)	Activity coefficient (AC) ₋₁	$R^2 = 0.994$	$R^2 = 0.994$	273.15–293.15
		$n = 3.15$	$T_0 = 118 \text{ K}$	
		$A' = -0.528$	$C' = -0.129$	
Glycerol + KCl (*)	Electrical conductivity (EC)	$B' = -0.008$	$D' = -0.144$	270.15–323.75
		$R^2 = 0.999$	$R^2 = 0.999$	
		$n = 3.26$	$T_0 = 119 \text{ K}$	
Water + LiCl (**)	(TN) at infinite dilution	$A' = +6.044$	$C' = +12.87$	273.15–373.15
		$B' = -0.134$	$D' = -2.479$	
		$R^2 = 0.999$	$R^2 = 0.999$	
		$n = 3.85$	$T_0 = 116 \text{ K}$	
		$A' = -0.927$	$C' = -0.741$	
		$B' = -0.001$	$D' = -0.064$	
		$R^2 = 0.990$	$R^2 = 0.997$	

*[37]

**[43]

Fig. 6 Fitting of experimental data of (TN) to power law

Fig. 9 Fitting of experimental data of (AC) to Vogel–Tamann–Fulcher equation

Fig. 7 Fitting of experimental data of (TN) to Vogel–Tamann–Fulcher equation

Fig. 8 Fitting of experimental data of activity coefficient (AC) to power law

$$\text{Ln}(\text{TN}) = A' + B' \left(\frac{1000}{T} \right)^n \quad (8)$$

$$\text{Ln}(\text{TN}) = C' + D' \left[\frac{1000}{(T - T_0)} \right] \quad (9)$$

It can be seen that, considering the accuracy of the results, the values of n and T_0 for TN, activity coefficient (AC) and electrical conductivity (EC) have close values indicating that they are all controlled by the same fundamental process. Besides, the values of A' , B' , C' , D' of both TN and EC are quite comparable, but not very much with those of AC. Indeed, the values of n and T_0 of aqueous solutions are remarkably close to glycerol, suggesting that both solvents being hydrogen-bonded behave similarly and exhibit the same transport properties, though water is one thousand times less viscous than glycerol.

4.2 Polymer membrane data

The transference numbers of different salt ions in solution are quite different from each other. However, in an ion exchange membrane, there are the fixed ions, in addition to the mobile counter-ions of the electrolyte. The fixed ions (co-ions) do not contribute to the transport of electrical charges. Their transference number is theoretically zero. Furthermore, the concentration of the counter-ions is much lower than that of the co-ions. Their concentration in the membrane determines the permselectivity of a membrane [45].

4.2.1 Optimization of TN of Li^+ using Hittorf's method

The optimization of lithium through the cation exchange membrane (Nafion) using Hittorf's method has been investigated. In effect, the TN of Li^+ was calculated on the basis of Faraday's second law (Eq. 6). During 30 min of electrolysis, the applied voltage was systematically constant and fixed at value 5 V. However, the current fluctuated a little bit indicating the small changes occurring during the

Fig. 10 Optimization of lithium transfer through the cation exchange membrane (Nafion) using Hittorf's method: concentration of lithium in cathode compartment and corresponding transport number

Table 4 Quantities of lithium metal involved in experiments using the three methods (mg)

Bruce–Vincent technique	Concentration cell with junction	Hittorf's method
690	517	80

electrolysis and resulting in concentration polarization and decrease in the electric resistance of the membrane.

The values of the TN are calculated using Eq. 7. As shown in Fig. 10, the TN varies linearly with concentration of Li-ion in the cathode compartment as predicted by Faraday's second law. The maximum transfer of Li⁺ through the membrane necessitates the transport of Li⁺ (i.e., 11.56 mmol L⁻¹), yielding a TN approximately equal to unity, while the minimum transfer requires just a tenth (i.e., 1.27 mmol L⁻¹). The transport of Li-ion can be achieved through the polymer ionic exchange membrane nafion 117 via its polyanion sulfonic site SO₃⁻, though the higher viscosity of glycerol. These data are consistent with those previously reported in the literature using higher dielectric constant solvent such as N.Methyl.Formamide ($\epsilon_r = 182$) [46, 47]. Unfortunately, in low temperature, the Hittorf's cell cannot be suitable for measuring the transport number because it displays higher resistance that opposes to the migration of the counter Li⁺ through the polymeric membrane.

In addition, from an initial concentration of 100 mmol L⁻¹, the TNs of Li⁺ are 0.395 and 0.543 for concentration cell method and Bruce–Vincent technique, respectively, whereas for the Hittorf's method, the TN could easily reach the highest value (≈ 1.0). This method proves that the use of a cation exchange membrane in

a Li-ion battery is really advantageous since it yields the largest transport number that can reduce significantly the concentration gradient during charge–discharge steps of the battery [16, 17]. The quantities of Li⁺ involved in the experiment for each method are given in Table 4. It is obvious that Hittorf's method requires the lowest quantity of Li-ion and achieves the highest TN. However, this technique seems to be inappropriate in low temperature where the Hittorf's cell displays higher resistance that opposes to the transfer of Li⁺ through the polymeric membrane. As shown previously, a strategy was undertaken to find electrolyte solutions of an optimal composition for the conflicting objectives: maximizing electrical conductivity and minimizing conductive lithium salt content. These objectives are representatives of the aims: maximization of performance and reduction costs of lithium-based salts used in Li-ion batteries [6].

Due to its considerably higher ionic conductivity at ambient temperature, high Li-ion transference number (≈ 1) and thermal stability, the inorganic Li-ion conductor, NASICON-type superionic conducting glass ceramic, like Li_{1+x}Al_xGe_{2-x}(PO₄)₃ (LAGP), was synthesized. The introduction of an ionic liquid (IL) into the interlayer between LAGP solid electrolyte and the lithium anode for a solid-state battery (SSB), that enhanced considerably the transport of Li⁺. This novel material showed therefore a great promise to meet the practical demand for a SSB. However, it is very expensive since it utilized the high-cost IL [48]. The material LiXGe containing ion-conductive hybrid skin for high-rate lithium metal anode has been also synthesized out and proved its efficiency for the enhancement of electrical power generation in novel solid-state lithium batteries [49]. So, the synthesis of the new polymer-based electrolytes using the same procedure as Xiong and Liu may be a good alternative to conceive high performance and low-cost Li-ion batteries in the future.

4.2.2 Current–voltage characteristics

In the systems studied (i.e., solution/membrane interface) with the nafion 117 membrane, the current–voltage curves obtained are composed of three characteristic parts:

- A first linear part at low current which expressed an ohmic response of the M⁺Cl⁻/Nafion 117/M⁺Cl⁻ interface (M⁺ $\equiv$ Li⁺, K⁺).
- A second part in the form of a *plateau* which corresponds to the limiting current which is due to the polarization of concentration at the membrane interface.
- A third part which corresponds to a new increase in current probably due to the dissociation of the solvent.

Fig. 11 Current–voltage characteristics of Nafion membrane equilibrated with LiCl solution 100 mmol L^{−1}; limiting current = 1.5 mA

Fig. 12 Current–voltage characteristics of Nafion membrane equilibrated with KCl solution 100 mmol L^{−1}; limiting current = 60 mA

Indeed, for currents lower than the limit current, it is the metal cations (M^+) which ensure the transport through the membrane. However, when the current becomes of the same order as the limiting current, a large voltage variation corresponds only to a small current variation; it is therefore the level of the limiting current, which indicates the polarization of the concentration. Furthermore, as shown in Figs. 11 and 12, the value of the limiting current in the presence of Li^+ (1.5 mA) is much lower than that of K^+ (60 mA), qualitatively in good agreement with previous studies using 10 mmol L^{−1} of sodium cation Na^+ [50]. Nevertheless, we attribute this large decrease between the values of the two ions Li^+ and K^+ , to the difference in their standard hydration Gibbs energies ($\Delta G_{Li^+}^0 = -481 \text{ kJ mol}^{-1}$, $\Delta G_{K^+}^0 = -304 \text{ kJ mol}^{-1}$), diffusion coefficients ($D_{Li^+} = 10.29 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, $D_{K^+} = 19.57 \times 10^{-10}$

$\text{m}^2 \text{ s}^{-1}$) and ionic mobilities ($u_{Li^+} = 2.56 \times 10^{-4} \text{ cm}^2/\text{Vs}$, $u_{K^+} = 3.29 \times 10^{-4} \text{ cm}^2/\text{Vs}$) [8, 51, 52]. Although Li^+ is more energetically efficient at oxidation at the anode, it is however a source of polarization of concentration in the diffusion layer adjacent to the membrane in the Li-ion battery and consequently compromises its performance. For this reason, it is better to use an ionic polymer instead of a solution, as a separator.

5 Conclusion

In this work, we studied the transport properties of Li^+ in green nonaqueous solutions and polymer ionic exchange membranes with an attempt to elaborate in future a novel ecological Li-ion battery. It has been therefore shown that both the concentration cell and Bruce–Vincent method can be successfully used to yield TN of Li^+ in glycerol that are close to each other. The results were successfully compared to recent investigation with polyelectrolyte systems by using molecular dynamics simulations. Furthermore, on a fundamental level, the data of temperature dependence using the concentration cell method gave the values of the power law and VTF fitting parameters n and T_0 for TN, activity coefficient and electrical conductivity that are close to each other. They, therefore, indicated that all these three transport properties were controlled by the same fundamental process. Besides, the data suggested that both hydrogen-bonded solvents glycerol and water behaved similarly and exhibited the same transport properties, though glycerol is very much viscous than water (i.e., 1000 times greater).

In addition, the Hittorf's method seemed to yield the highest TN and consumed less Li^+ . Hence, the conception of Li-ion battery with the Nafion membrane as a solid polymer electrolyte is very beneficial for delivering higher electric energy. However, the current–voltage characteristic yielded low limiting current density, indicating that the polarization was more pronounced with such light cation (i.e., Li^+). Moreover, the use of the membrane was inappropriate at low temperature where the resistance of the cell became higher especially in the presence with viscous glycerol that opposed to the transport of Li-ion through the ionic exchanger.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

References

- Huang B, Pan SuX, An L (2018) Recycling of lithium-ion batteries: recent advances and perspectives. *J Power Sources* 399:274–286. <https://doi.org/10.1016/j.jpowsour.2018.07.116>
- Lopez J, Gonzalez M, Viera J-C, Blanco C (2004) Fast-charge in lithium-ion batteries for portable applications. In: INTELEC, 26th annual international telecommunications energy conference, Chicago, IL, USA. <https://doi.org/10.1109/intelec.2004.1401427>
- Wakihara M (2001) Recent developments in lithium-ion batteries. *Mater Sci Eng R33*:109–134
- Masurkar N, Babu G, Porchelvan S, Mohana L, Arava R (2018) Millimeter-scale lithium-ion battery packaging for high-temperature sensing applications. *J Power Sources* 399:179–185. <https://doi.org/10.1016/j.jpowsour.2018.07.077>
- Zubi G, Dufo-López R, Carvalho M, Pasaoglu G (2018) The lithium-ion battery: state of the art and future perspectives. *Renew Sust Energy Rev* 89:292–308. <https://doi.org/10.1016/j.rser.2018.03.002>
- Neuhaus J, Forte E, Harbou E, Hasse H (2018) Electrical conductivity of solutions of lithium bis(fluoro sulfonyl)imide in mixed organic solvents and multi-objective solvent optimization for lithium-ion-batteries. *J Power Sources* 398:215–223. <https://doi.org/10.1016/j.jpowsour.2018.07.065>
- Neuhaus J, Harbou E, Hasse H (2020) Spectroscopic investigations of solutions of lithium bis(fluorosulfonyl) imide (LiFSI) in valeronitrile. *Polyhedron* 183:114458. <https://doi.org/10.1016/j.poly.2020.114458>
- Izutsu K (2009) *Electrochemistry in nonaqueous solution*, 2nd revised edn. Wiley-VCH, Weinheim
- Liu Q, Liu Y, Jiao X, Song Z, Sadd M, Xu X, Matic A, Xiong S, Song J (2019) Enhanced ionic conductivity and interface stability of hybrid solid-state polymer electrolyte for rechargeable lithium metal batteries. *Energy Storage Mater* 23:105–111. <https://doi.org/10.1016/j.ensm.2019.05.023>
- Howell F-S, Moynihan C-T, Macedo P-B (1984) Electrical relaxations in mixtures of lithium chloride and glycerol. *Bull Chem Soc Jpn* 57:652–661. <https://doi.org/10.1246/bcsj.57.652>
- Meyer W-H (1998) Polymer electrolytes for lithium-ion batteries. *Adv Mater* 10:439–448. [https://doi.org/10.1002/\(SICI\)1521-4095\(199804\)10:6<3c439:AID-ADMA439%3e3.0.CO;2-I](https://doi.org/10.1002/(SICI)1521-4095(199804)10:6<3c439:AID-ADMA439%3e3.0.CO;2-I)
- Pagot G, Tonello S, Vezzù K, Di Noto V (2018) A new glass-forming electrolyte based on lithium glycerolate. *Batteries*. <https://doi.org/10.3390/batteries4030041>
- Fong K-D, Self J, Diederichsen K-M, Wood B-M, McCloskey B-D, Persson K-A (2019) Ion transport and the true transference number in nonaqueous polyelectrolyte solutions for lithium ion batteries. *ACS Cent Sci* 5(7):1250–1260. <https://doi.org/10.1021/acscentsci.9b00406>
- Diederichsen K-M, McShane E-J, McCloskey B-D (2017) Promising routes to a high Li⁺ transference number electrolyte for lithium ion batteries. *ACS Energy Lett* 2(11):2563–2575
- Elia G-A, Ulissi U, Mueller F, Reiter J (2016) A new long life lithium ion battery with enhanced electrode/electrolyte interface by using an ionic liquid solution. *Chem Eur J* 22(20):6808–6814. <https://doi.org/10.1002/chem.201505192>
- Valøen L-O, Reimers J-N (2005) Transport properties of LiPF₆-based li-ion battery electrolytes. *J Electrochem Soc* 152(5):882–891. <https://doi.org/10.1149/1.1872737>
- Stephan M, Nahm K-S (2006) Review on composite polymer electrolytes for lithium batteries. *Polymer* 47:5952–5964. <https://doi.org/10.1016/j.polymer.2006.05.069>
- Ye L, Feng Z (2010) Polymer electrolytes as solid solvents and their applications. *Polym Electrolytes*. <https://doi.org/10.1533/9781845699772.2.550>
- Barthel J, Gores H-J, Schmeer G, Wachter R (1983) Non-aqueous electrolyte solutions in chemistry and modern technology. In: Boschke F-I (ed) *Topics in current chemistry*. Springer, Berlin, pp 59–60
- Benouar A, Kameche M, Bouhlala M-A (2015) Molar conductivities of concentrated lithium chloride-glycerol solutions at low and high temperatures: application of quasi-lattice model. *Phys Chem Liq* 54(1):62–73. <https://doi.org/10.1080/00319104.2015.1068660>
- Bouhlala M-A, Kameche M, Tadjia Benouar A (2018) Chitosan hydrogel-based electrolyte for clean and biodegradable batteries: energetic and conductometric studies. *Phys Chem Liq* 56(2):266–278. <https://doi.org/10.1080/00319104.2017.1337767>
- Brown A-S, Macinnes D-A (1935) The determination of activity coefficients from the potentials of concentration cells with transference. I. Sodium chloride at 25°. *J Am Chem Soc* 57(7):1356–1362. <https://doi.org/10.1021/ja01310a055>
- Champeny D-C, Comert H (1988) Transference number and activity coefficients of solutions of KCl and NaCl in glycerol using concentration cells. *Phys Chem Liq* 18(1):43–52. <https://doi.org/10.1080/00319108808078576>
- Blanco M-C, Champeny D-C, Kameche M (1989) Transference numbers and activity coefficients of some alkali metal halides in ethylene glycol, using concentration cells. *Phys Chem Liq* 20(2–3):93–103. <https://doi.org/10.1080/00319108908036396>
- Evans J, Vincent C-A, Bruce P-G (1987) Electrochemical measurement of transference numbers in polymer electrolytes. *Polymer* 28:2324–2328. [https://doi.org/10.1016/0032-3861\(87\)90394-6](https://doi.org/10.1016/0032-3861(87)90394-6)
- Bruce P-G, Vincent C-A (1987) Steady state current flow in solid binary electrolyte cells. *J Electroanal Chem Interfacial Electrochem* 225(1–2):1–17. [https://doi.org/10.1016/0022-0728\(87\)80001-3](https://doi.org/10.1016/0022-0728(87)80001-3)
- Zhao J, Wang L, He X, Wan C, Jiang C (2008) Determination of lithium-ion transference numbers in LiPF₆-PC solutions based on electrochemical polarization and NMR measurements. *J Electrochem Soc* 155(4):A292–A296. <https://doi.org/10.1149/1.2837832>
- Vink H-A (1984) New modified Hittorf method for the determination of transport numbers in polyelectrolyte solutions. *J Chem Soc, Faraday Trans* 80(5):1297–1304. <https://doi.org/10.1039/f19848001297>
- Kontturi K, Ekman A, Forsell P-A (1985) Method for determination of transport numbers in ion exchange membranes. *Acta Chem Scand* 39(4):273–277. <https://doi.org/10.3891/acta.chem.scand.39a-0273>
- Yang M, Hou J (2012) Membranes in lithium-ion battery. *Membranes* 2:367–383. <https://doi.org/10.3390/membranes2030367>
- Spiegler K-S (1971) Polarization at ion exchange membrane-solution interfaces. *Desalination* 9:367–385. [https://doi.org/10.1016/0011-9164\(71\)80005-X](https://doi.org/10.1016/0011-9164(71)80005-X)
- Forgacs C, Ishibashi N, Leibovitz J (1972) Polarization at ion exchange membranes in electrodialysis. *Desalination* 10(2):181–214. [https://doi.org/10.1016/S0011-9164\(00\)80085-5](https://doi.org/10.1016/S0011-9164(00)80085-5)
- Tanaka Y (1991) Concentration polarisation in ionic exchange membrane. *J Membr Sci* 57(2–3):217–235. [https://doi.org/10.1016/S0376-7388\(00\)80680-8](https://doi.org/10.1016/S0376-7388(00)80680-8)
- Aguilella V-M, Mafab S, Manzanares J-A, Pellicer J (1991) Current-voltage curves for ion-exchange membranes. Contributions to the total potential drop. *J Membr Sci* 61:177–190
- Tanaka Y (2004) Concentration polarization in ion-exchange membrane electrodialysis. The events arising in an unforced flowing solution in a desalting cell. *J Membr Sci* 244(1–2):1–16. <https://doi.org/10.1016/j.memsci.2004.02.041>

36. Hamani H, Lahcene D, Boufeldja C, Haddou B, Kameche M, Innocent C, Derriche Z (2011) Study of fouling of a cation exchange membrane with a surfactant using voltamperometry. *Sep Sci Technol* 46(15):2322–2331. <https://doi.org/10.1080/01496395.2011.595031>
37. Champeney D-C, Ould Kaddour F (1984) Ionic mobility and dielectric relaxation in supercooled liquid KCl-glycerol solutions. *Mol Phys* 52(3):509–523. <https://doi.org/10.1080/0026897840101371>
38. Hammadi A, Champeney D-C (1999) Ionic mobility and dielectric relaxation in glass-forming mixtures of sodium chloride and glycerol. *J Sol Chem* 28(1):21–34. <https://doi.org/10.1023/A:1021747223332>
39. Ferloni P, Chiodelli G, Magistris A, Sanesi M (1986) Ion transport and thermal properties of poly(ethyleneoxide)-LiClO₄ polyelectrolytes. *Solid State Ionics* 18–19:265–270. [https://doi.org/10.1016/0167-2738\(86\)90124-4](https://doi.org/10.1016/0167-2738(86)90124-4)
40. Watanabe M, Nagaro S, Sanui K, Ogata N (1988) Estimation of Li⁺ transport number in polymer electrolytes by the combination of complex impedance and potentiostatic polarization measurements. *Solid State Ionics* 28–30(Part 2):911–917. [https://doi.org/10.1016/0167-2738\(88\)90303-7](https://doi.org/10.1016/0167-2738(88)90303-7)
41. MacInnes D-A, Dole M (1931) The transference numbers of potassium chloride. New determinations by the Hittorf method and a comparison with results obtained by the moving boundary method. *J Appl Chem Soc* 53(4):1357–1364. <https://doi.org/10.1021/ja01355a025>
42. Munshi M-Z-A, Nguyen S, Owens B-B (1988) Measurement of Li⁺ ion transport numbers in poly(ethyleneoxide)-LiX complexes. *Polym J* 20(7):597–602. <https://doi.org/10.1295/polymj.20.597>
43. Horvath A-L (1985) Handbook of aqueous electrolyte solutions: physical properties, estimation and correlation methods. Ellis Harwood Chichester, Chichester
44. Diederichsen K-M, Buss H-G, McCloskey B-D (2017) The compensation effect in the Vogel–Tammann–Fulcher (VTF) equation for polymer-based electrolytes. *Macromolecules* 50(10):3831–3840. <https://doi.org/10.1021/acs.macromol.7b00423>
45. Strathmann H (2004) Ion-exchange membrane separation processes, membrane science and technology series 9, 1st edn. Elsevier, Amsterdam
46. Innocent C, Huguet P, Bribes J-L, Pourcelly G, Kameche M (2001) Characterisation of cation exchange membrane in hydro-organic media by electrochemistry and Raman spectroscopy. *Phys Chem Chem Phys* 3:1481–1485. <https://doi.org/10.1039/B008318F>
47. Kameche M, Innocent C (2002) Caractérisation de membranes échangeuses d'ions en milieux hydro-organiques. *Entropie* 237:8–11
48. Xiong S, Liu Y, Jankowski P, Liu Q, Nitze F, Xie K, Song J, Matic A (2020) Design of a multifunctional interlayer for NASICON-based solid-state Li metal batteries. *Adv Funct Mater*. <https://doi.org/10.1002/adfm.202001444>
49. Liu Y, Xu X, Jiao X, Guo L, Song Z, Xiong S, Song Jiangxuan (2019) Li_xGe containing ion-conductive hybrid skin for high rate lithium metal anode. *Chem Eng J* 371:294–300. <https://doi.org/10.1016/j.cej.2019.04.068>
50. Amir Mansoor A, Mustakeem M, Nedela D (2017) Study the transport properties of anion and cation exchange membranes toward various ions using chronopotentiometry. *Iran J Chem Chem Eng* 36(2):81–87
51. Buffle J, Zhang Z, Startchev K (2007) Metal flux and dynamic speciation at (bio) interfaces. Part I: critical evaluation and compilation of physico-chemical parameters for complexes with simple ligands and fulvic/humic substances. *Environ Sci Technol* 41(22):7609–7620. <https://doi.org/10.1021/es070702p>
52. Lee S-H, Rasaiah J-C (1994) Molecular dynamics simulation of ionic mobility I Alkali metal cations in water at 25°C. *J Chem Phys* 101(8):6964–6974

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