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Ionic conductivity of lithium conducting SiO_2 gels at room temperature

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Fresh silica gels have been used as hosts for liquid organic lithium electrolytes. The residual liquid inside the fresh gels was exchanged by the solutions of selected lithium salts (lithium hexafluorophosphate, lithium tetrafluoroborate) in organic solvents: propylene carbonate (PC), dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), 1,2-diethoxyethane (DEE) and dimethyl carbonate (DMC). The immersion of the gels in solutions based on DEE, DMF and DMC leads to the fast deterioration of the gels. The gels immersed in the solutions based on PC and DMSO exhibit stable conductivities in the range of $10^{-3}\,S\,cm^{-1}$ at room temperature. That conductivity is close to the conductivity of the corresponding lithium salt solutions.

1. Introduction

Research in the field of rechargeable lithium batteries has for many years been stimulated by the demand of developing new lightweight, reliable, inexpensive cells with long lifetime under operation at ambient temperature [1]. The search for new electrolytes is one of the main directions of those investigations.

From among lithium conducting electrolytes the highest conductivities and, so far, the best performance in the laboratory cells have been reported for liquid solutions of selected lithium salts (e.g., $LiBF_4$ or $LiPF_6$) in organic solvents like propylene carbonate (PC) [2] or solvent mixtures (e.g. dimethyl carbonate (DMC):ethylene carbonate (EC)) [3]. The best of these electrolytes exhibit room temperature conductivities close to $10^{-2}\,S\,cm^{-1}$ and do not deteriorate during cell charging at potentials up to about 5 V (vs Li/Li^+) [3]. One of the important disadvantages of these electrolytes is, however, the necessity of the use of a separator.

So far the idea of circumventing this drawback by using solid lithium electrolytes (e.g., LISICON, $Li\beta''$-alumina or amorphous lithium conducting thin films) has failed because of their too low conductivities at room temperature ($\leq 10^{-6}\,S\,cm^{-1}$) and/or reactivity between electrolyte and Li electrode [4, 5, 6].

At the end of 1970s, new hope for developing better lithium batteries was awakened by the idea of using thin-layer self-supporting polymer electrolytes, based mainly on complexes formed between poly(ethylene oxide) (PEO) and selected lithium salts [7]. Unfortunately, it has been found that the better mechanical properties of these semisolid electrolytes cannot compensate for their poor conductivity at room temperature (usually 10^{-9}–$10^{-5}\,S\,cm^{-1}$ [8]). Moreover, the polymer electrolyte modifications (e.g., replacing PEO by polyphosphazenes [9] or using polymer blends [10]), leading to higher room temperature conductivity, cause considerable deterioration of their mechanical properties.

More recently, apart from research on optimizing properties of liquid electrolytes, there have been several attempts to use an alternative 'hybrid' solid–liquid electrolytes consisting of a supporting solid organic gel matrix and a liquid lithium conducting solution penetrating the matrix [11–13]. Also, there have been attempts to prepare new solid lithium conducting electrolytes based on SiO_2 using sol–gel process [14–16]. Lithium salts ($LiNO_3$, LiCl) were added at the beginning of the sol–gel process. The sol–gel process has also been used, among other applications, in the field of solid state ionics [17] but mainly to prepare good insertion materials for positive electrodes (e.g., V_2O_5 [18]) for lithium batteries. Summary accounts of the state-of-the art for the rapidly developing sol–gel process in science and technology are available in [19–21].

In our approach, it was intended to utilize the unique properties of inorganic gels based on silica, mainly their high porosity (~40–60 vol %) and the possibility of forming thin layers [19], to prepare a novel type of lithium conducting electrolyte. It is proposed to achieve this goal by exchanging the residual liquid, present within gels throughout the sol-to-gel transformation, by a liquid electrolyte with good lithium conduction. This work has been encouraged by results of previous studies which have shown that it is possible to almost completely exchange a liquid byproduct of hydrolysis and condensation reactions [19], accompanying the gelation of silica sols (a mixture of H_2O and methanol or

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ethanol), by other liquids, for example, dimethysulfoxide (DMSO) or dimethyl formamide (DMF) [22].

We report here the results of electrical conductivity measurements of monolith tetramethoxysilane (TMOS)-based gels in which the original liquid phase was exchanged by solutions of lithium salts ($LiBF_4$, $LiPF_6$) in selected organic solvents: PC, DMF, DMC, DMSO and 1,2-diethoxyethane (DEE). The choice of solvents and lithium salts was based on the analysis of literature data on liquid electrolyte performances (e.g., [1, 3, 23]).

2. Experimental details

The general outline of a procedure applied here for preparation of gels can be classified as a single-step acidic catalysed process [19]. Starting chemicals: TMOS (Aldrich, > 98%), double-distilled water, methanol (Merck, 99.8%) were used without further purification. The appropriate amounts of chemicals corresponding to molar composition of TMOS:H_2O:HCl:MeOH = 1:4:0.0005:3 were prepared in two parts: first, TMOS + ½MeOH, and second, H_2O + HCl + ½MeOH. In most cases 10^{-5} M pyranine (hydroxypyrene 1,3,6 trisulfonic acid or HPS, Fluka, > 95%) was added to make possible a further monitoring of the relative water content within sols/gels by the spectrofluorometric technique [24, 25]. The components were stirred for 10 min at 0 °C in a beaker covered by Parafilm. It was found that the pH values for as-received sols were between 2 and 3, that is, close to isoelectric point of silica (pH ~2 [19]). About 4–5 ml volumes of resulting sols were put into polystyrene cuvettes, covered by Parafilm to prevent rapid evaporation of water and/or methanol and stored at room temperature up to and beyond the point of gelation. Usually this occurred 12 to 14 days after sol preparation and was followed by shrinkage of the gel. It was found by spectrofluorometric measurements using a Shimadzu RF-50301 PC spectrofluorometer, that the water to methanol molar ratio in the residual liquid inside gel pores is, at this stage, close to 30:70. To exchange this liquid by a good liquid electrolyte, several solutions of lithium salts were prepared: namely, $LiBF_4$ (Merck, 98%), $LiPF_6$ (Aldrich, 98%), LiI (Merck, > 99%) in the following solvents: PC (Merck, p.a), DMSO (Merck, p.a.), DMF (Merck, p.a.), DMC (Aldrich, > 99%). These chemicals were used just after delivery and were not further purified. All air-sensitive chemicals were stored in original bottles inside a moisture- and oxygen-free glove-box flushed by dry nitrogen. Preparation of solutions, exchanges and impedance measurements were all performed inside the glove-box.

Slightly shrunken gels (transparent monoliths of dimensions about 0.8 cm × 0.8 cm × 2.5 cm) were put into 40 ml of appropriate solutions and kept there for at least three weeks in sealed bottles inside the glove box prior to electrical conductivity measurements. The gels were transparent with no visible cracks. However, they were vulnerable to external mechanical stresses. Upon stress cracks formed rapidly and the gels could be destroyed. The investigations of the ionic conductivity of lithium solutions, as-prepared gels and gels after immersion in lithium solutions were carried out using the two-probe impedance spectroscopy method. The impedance spectra were taken at room temperature using a computer-controlled impedance analyser HP 4192A within the frequency range 5 Hz to 10 MHz at 10 points per decade. The amplitude of the a.c. signal was set to 30 mV. Electrical conductivity of as-prepared sols prior to and slightly beyond the gelation point was measured in a cell with two gold electrodes (1 cm × 1 cm) placed at 1 cm distance from each other. Lithium solutions were placed for measurements inside a calibrated cell with two platinum electrodes. The impedance spectra of gels before and after immersion were measured using a holder [22] with two platinum-coated discs slightly spring-loaded against gel surfaces. After mounting the gels in the holder, their impedance spectra were taken for 1 to 30 days every 15 to 180 min depending on the change with time. After the measurements the gels were replaced in the same, or fresh solutions to continue the exchange. The impedance spectra were numerically analysed, by an equivalent electrical circuit model [26], using the FIRDAC computer package [27].

Preliminary investigations of the extent of exchange in gels, using spectrofluorometric techniques with pyranine as a photoprobe were carried out. The results suggest that the water content in the liquid in the gel pores drops after the exchanges to below 5% (of the volume of the liquid).

3. Results and discussion

3.1. *Electrical conductivity of as-prepared gels*

The intrinsic electrical conductivity of fresh gels just after the gelation point does not vary substantially from that of the initial sols (Fig. 1) and is close to 2 to $3 \times 10^{-5}\,\mathrm{S\,cm^{-1}}$ at 20 °C. The apparent decrease in

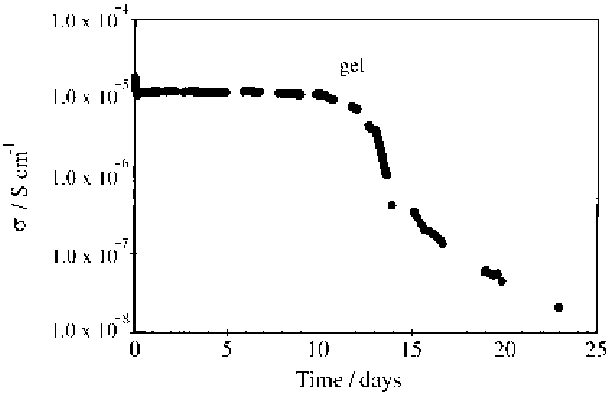

Fig. 1. Time dependence of electrical conductivity of as-prepared TMOS:H_2O:HCl:MeOH = 1:4:0.0005:3 sol from the preparation to beyond the point of gelation.

conductivity after the 13th day was found to be due to the gradual loss of the electrical contact between a shrinking gel and the gold electrodes and not to a decrease in the intrinsic conductivity of the gel. It was found that only after a much longer time, when the gel had shrunk to about 20% of the initial volume, did its conductivity drop to much lower values (~10^{-8} S cm^{-1}). The relatively high conductivity of sols and fresh gels is ascribed to the presence of mobile protonic charge carriers [22, 28], and also to other possible charged species, for example, Si–O$^-$ anions, present at pH values above the isoelectric point of silica [19]. Further evidence for high mobility of non-protonic species within gels was given by Gits-Léon *et al.* [29], who found that the diffusion coefficient for NaCl in a silica gel is only slightly lower than in pure water. Since it is well established that at the gelation point most of the properties (apart from viscosity and related quantities) and structural units of silica sols/gels do not undergo substantial changes [19] it is not surprising that the electric conductivity does not change as a result of gelation. A gel at that stage can be considered as a relatively open network with a continuous liquid phase allowing relatively fast transport [19]. At the gelation point as little as 20% of the silicate is incorporated in the infinite spanning cluster [30].

3.2. *Electrical conductivity of lithium containing solutions*

Electrical conductivities of solutions of selected lithium salts in organic solvents were determined from the values of the resistance parameter, *R*, obtained as a result of numerical fitting of the measured impedance spectra (Fig. 2). Since impedance spectra consisted of a slightly depressed semicircle (at higher frequencies) and a linear spur (at lower frequencies) we used a simple electrical equivalent circuit (shown as an inset in Fig. 2) to fit the data. In this circuit, used for all solutions under study, a parameter *R* has been ascribed to the bulk resistance of the solution, *C* to the geometrical capacity and CPE$_1$ to a nonideal capacity of the electrode double layer. Values of room temperature conductivities for selected solutions are listed in Table 1. The conductivity values of prepared solutions did not differ considerably from those published in papers on liquid organic lithium electrolytes [1, 3, 23] and were (with exception of solutions based on DEE and DMC) in the range from 10^{-3} to 10^{-2} S cm^{-1}.

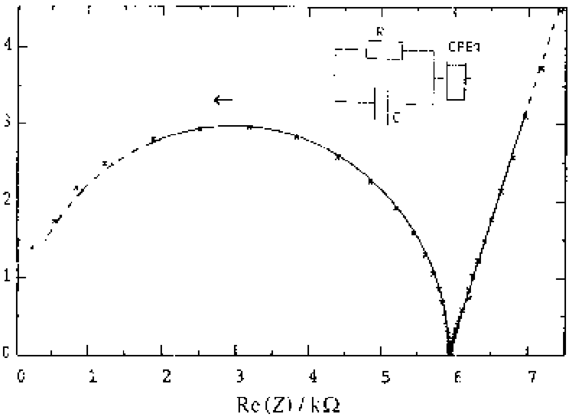

Fig. 2. Impedance spectrum for 0.2 M $LiBF_4$–DMC solution, with an inserted electrical equivalent circuit. Points denote experimental data; solid line corresponds to numerical fit. The arrow shows the increasing frequency.

Table 1. Electrical conductivities of selected solutions of lithium salts at room temperature

Solution	*Conductivity*/S cm^{-1}
0.2 M $LiBF_4$–DMF	7.3×10^{-3}
0.2 M $LiPF_6$–DMSO	4.9×10^{-3}
0.2 M $LiBF_4$–PC	2.7×10^{-3}
0.2 M LiI–PC	2.7×10^{-3}
1 M LiBr–PC	1.6×10^{-3}
0.2 M $LiPF_6$–PC	6.0×10^{-4}
1 M $LiBF_4$–DEE	4.6×10^{-4}
0.6 M $LiBF_4$–DEE	1.0×10^{-4}
0.2 M $LiBF_4$–DMC	4.8×10^{-5}

3.3. *Electrical conductivity of gels after immersion*

The immersion of gels in lithium containing solutions caused changes of mechanical integrity and ionic conductivity which greatly depended on the given solution.

The electrical conductivity of exchanged gels was determined from impedance spectra taking into account geometrical factors of the gels. These spectra were taken repeatedly (typically, every 15 min or 1 h, but not only so). After some time samples were taken out of a holder and placed again into a corresponding solution, immersed for some time, then removed and measured. The procedure was repeated several times.

It was found that the substitution of the original liquid by solutions based on DEE, DMC, and to a lesser extent on DMF, led to irreversible chemical reactions. These changes are reflected by the change of the impedance spectra with time. Reaction products appeared as white powders on the gel surfaces and caused a fast drop of electrical conductivity (Fig. 3) from the initial value close to that of the solution, down to beyond limits of our experimental setup (i.e., resistances higher than 10^7 Ω). This conductivity decrease was accompanied by the mechanical deterioration of the gels. The conductivity of solutions themselves did not change as a result of immersion. It is worthwhile noting that the immersion of gels in pure solvents, DMC, DEE or DMF, did not lead to similar changes.

It was observed that the gels immersed in solutions based on PC, and DMSO did not exhibit any visible deterioration in mechanical integrity (samples remained transparent with no visible cracks). In these cases the immersion led to a considerable increase of the conductivity from about 10^{-5} S cm^{-1} for fresh gels to stable values comparable to those of the solutions,

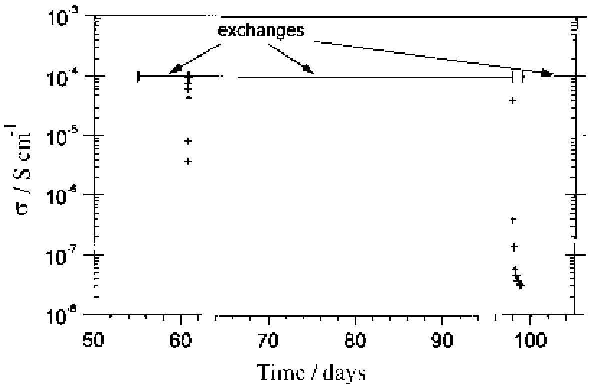

Fig. 3. Time dependence of electrical conductivity of a gel immersed in 0.6 M $LiBF_4$–DEE. (crosses denote conductivity of a gel after exchange, lengths of solid horizontal lines correspond to times of exchanges and their vertical positions to initial conductivity of solution.

about 10^{-3} S cm^{-1} (Fig. 4). The conductivity values of the solutions did not change as a result of the exchange. The impedance spectra were essentially the same as for the corresponding solutions (i.e., same as in Fig. 2). Therefore, we used the same electrical equivalent circuit. Neither a deterioration of the gels nor cracks as the result of immersion in these solutions were observed. It should also be noted that a prolonged measurement of a gel outside a solution (even 40 days (Fig. 4)) did not cause degradation or shrinkage of the sample, whereas leaving a fresh gel in the same conditions led to considerable shrinkage. The latter result can partly be ascribed to a much lower evaporation rate of PC and DMSO compared to those of methanol or water. Values of the electrical conductivity of selected gels after exchanges together with those of corresponding solutions are listed in Table 2.

Data in Table 2 show that only the immersion of gels in solutions based on PC and DMSO results in gel materials of promising electrical conductivity.

4. Conclusions

It was found possible to exchange the residual liquid inside the pores of fresh gels based on TMOS, by selected nonaqueous lithium electrolytes. In the case of DMC, DEE and DMF-based solutions the chemical reactions between water, and/or OH^- groups present within the pores and solutions themselves led to irreversible degradation of the exchanged system.

In the case of PC and DMSO-based lithium electrolytes none of the above negative effects were observed. As a result of exchanges the conductivity of the gel increased to values close to those measured for

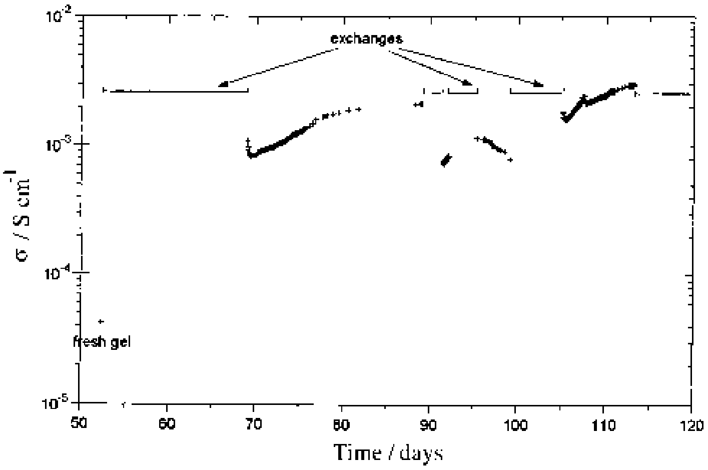

Fig. 4. Time dependence of electrical conductivity of a gel immersed in 0.2 M $LiBF_4$–PC (explanations as in Fig. 3).

Table 2. Electrical conductivities of selected gels after immersion in liquid lithium electrolytes at room temperature

Gel symbol	*Solution*	*Gel conductivity* /S cm^{-1}	*Conductivity of solution* /S cm^{-1}
E-5	0.2 M $LiPF_6$–DMSO	1.2×10^{-3}	4.8×10^{-3}
F-5	0.2 M $LiBF_4$–DMF	4.4×10^{-5}	7.1×10^{-3}
G-4	0.2 M $LiBF_4$–DMC	8.4×10^{-8}	4.8×10^{-5}
G-5	0.2 M $LiPF_6$–DMC	3.5×10^{-7}	4.1×10^{-4}
N-4	0.2 M LiI–PC	7.1×10^{-4}	2.7×10^{-3}
O-10	0.6 M $LiBF_4$–DEE	3.0×10^{-8}	1.0×10^{-4}
O-8	0.2 M $LiPF_6$–PC	7.9×10^{-4}	6.0×10^{-4}
P-10	0.2 M $LiBF_4$–PC	3.0×10^{-3}	2.6×10^{-3}
P-3	0.2 M $LiPF_6$–PC	3.1×10^{-4}	3.7×10^{-3}
R-10	0.2 M LiI–PC	5.6×10^{-4}	2.7×10^{-3}
R-2	0.6 M $LiBF_4$–DEE	1.5×10^{-7}	1.0×10^{-4}
S-3	0.2 M $LiPF_6$–DMC	5.9×10^{-9}	4.1×10^{-4}
S-4	0.2 M $LiPF_6$–PC	1.1×10^{-3}	6.0×10^{-4}

the immersion liquids and were stable for a long period of time.

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