A route to heat resistant solid membranes with performances of liquid electrolytes

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The confinement of ionic liquids within a porous silica matrix was performed by a one-step non-hydrolytic sol-gel route, leading to hybrid materials (called "ionogels") featuring both the mechanical and transparency properties of silica gels and the high ionic conductivity and thermal stability of ionic liquids.

The preparation of high-performance solid electrolytes is a major challenge for topical applications such as batteries and solar cells. Electrolytic membranes with medium range operating temperatures are needed in fuel cell applications.[1,2] Ionic liquids have attracted attention for a long time as effective electrolytes due to their high ionic conductivity and their wide electrochemical stability window (up to 6 V), combined with their non-volatility, high thermal stability and non-flammability.[3] Recently ionic liquids proved to be high-performance electrolytes in lithium batteries[4] and solar cells.[5–7] Moreover Brønsted acid–base ionic liquids have proved to meet the proton conductivity requirements for fuel cells.[8–10] These developments prompted numerous efforts to immobilize ionic liquids within quasi-solid systems.[11–15] Polymer membranes swollen with ionic liquids offer an attractive way to immobilize ionic liquids.[16–21] The superiority of these electrolyte membranes (which exhibit high proton transport at temperatures ranging from 370 to 420 K) over the classical water-swollen membranes lies on the non-volatility of ionic liquids; however the thermal stability of such systems remains limited by the organic nature of the polymer.

Herein we propose an alternative route based on the confinement of an ionic liquid within a thermally stable inorganic matrix. We prepared our ionogels through a well known non-hydrolytic sol-gel route,[22] using a mixture of tetramethoxysilane (TMOS), formic acid (FA) and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonylimide) [BMI][TFSI] (TMOS : FA : [BMI][TFSI] mole ratios 1 : 7.8 : 0.5; all reactants are liquid and miscible at room temperature). Gelation occurred after about 1.5 hours, and gels were aged for a few days at room temperature, or for a few minutes upon exposure to ultrasounds. Only a slight shrinkage related to the evolution of methyl formate was observed, and the gels were obtained as transparent pellets and rods. The mechanical characterization of the materials by a three-point bending technique indicated a Young modulus of about 63 MPa and a fracture strength of about 0.82 MPa.

The ionogels exhibited the same stability at high temperature as the ionic liquid alone: in both cases thermogravimetric analyses carried out at a slow heating rate (2 K min^{-1}) under air indicated the degradation of the ionic liquid only above 630 K. However it is noteworthy that differential scanning calorimetry (DSC) indicated a dramatic change in the behaviour of the confined ionic liquid when compared to the bulk one (Fig. 1): whereas the glass transition temperature at 184 K was kept, the exothermic peak at 236 K (attributed to crystallization) and the endothermic one at 267 K (melting) were not observed in the ionogels.

NMR experiments showed that ionogels did not produce any observable ^{1}H resonances at room temperature under liquid recording conditions (4.7 T). Solid state ^{1}H NMR usually requires a high spinning rate (35 kHz) at the magic angle (MAS). However, at 9.4 T a quite low spinning rate (0.4 kHz) was enough to recover high-resolution, thus indicating a quasi-liquid behaviour (Fig. 2). To our knowledge this is the first report on the effect of confinement of ionic liquids, in which confinement seems to lead to an intermediate state between liquid and solid.

Despite the restricted mobility reflected by the NMR experiments, the ionogels showed a conductivity of the same order of magnitude as that of bulk ionic liquids, that is respectively, about 3.10^{-2} S cm^{-1} and 8.10^{-2} S cm^{-1} at around 500 K.† Moreover the conductivity plots (Fig. 3) for both samples indicated similar Arrhenius activation energies (within the range 0.2–0.4 eV calculated in the range 250–400 K). These conductivities and activation energies were recovered on cooling after heating at 520 K. The conductivity of the ionogels was found to be stable over 20 h at 520 K (4.10^{-2} S cm^{-1}) which corresponded to the maximum conductivity.

The conducting behaviour of the ionogels is evidence of an interconnected porosity. In order to characterize the inorganic skeleton, the ionic liquid was washed out with acetonitrile. N_2 adsorption–desorption isotherms of the resulting pure silica

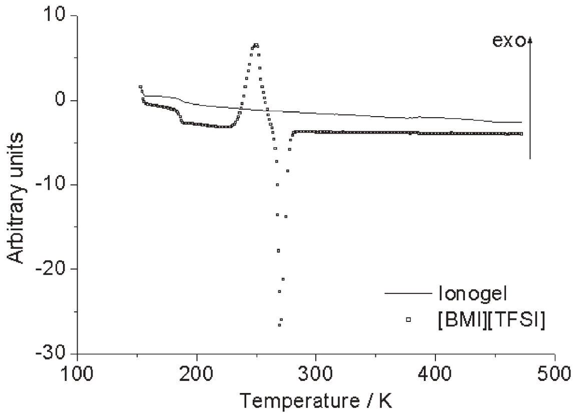

Fig. 1 DSC measurements: 2 K min^{-1} heating rate (after an initial cooling rate of -80 K min^{-1}); ambient atmosphere.

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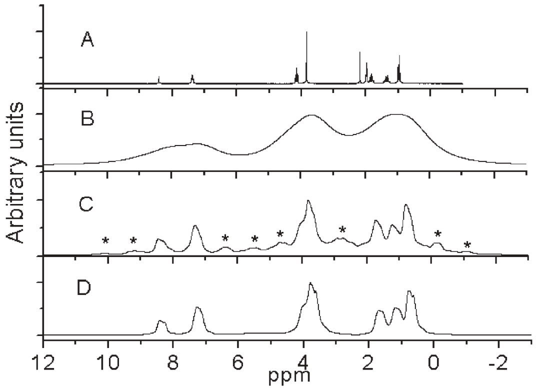

Fig. 2 ^{1}H NMR spectra. A: liquid state NMR, 4.7 T (in CD_3CN, relative to TMS: δ 8.41 (s, 1H, NC(H)N); 7.42 & 7.37 (2 s, 1 + 1 H, NC(H)C(H)N); 3.85 (s, 3H, NCH_3); 4.18 (q, 2H, NCH_2); 1.95 (t, 2H, NCC(H_2)); 1.38 (q, 2H, CC(H_2)CH_3); 1.01 (t, 3H, C–CH_3); B, C, D: solid state NMR, 9.4 T; B: no spinning; C : 0.4 kHz MAS (spinning side bands marked by *); D: 9 kHz MAS.

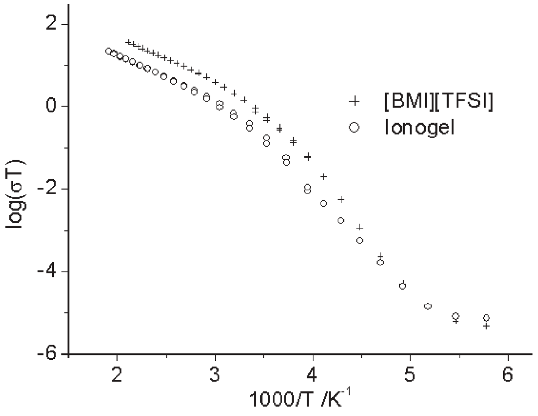

Fig. 3 Temperature dependence of the conductivity (cycling from 520 K to 180 K and back).

indicated a mesoporous solid (S_{BET} = 780 m^2 g^{-1}, V_{pore} = 1.50 cm^3 g^{-1}; $D_{pore} \approx$ 12 nm; Fig. 4) with values similar to those reported by Dai *et al.* who used ionic liquids as templates in the synthesis of silica aerogels.[23] Actually, based on the density of silica (about 2.0 g cm^{-3}), we can estimate a volume for the ionic liquid in our ionogels 3 times greater than the volume for the silica walls. Hence the ionogels can be pictured as two interpenetrating continuous networks of silica and organic salt intermingled at the molecular scale. Further dynamic information is required to get more insight into the mobility and the vibration modes of the molecular ions within the confined ionic liquid, into the influence of the interface, and finally into the mechanisms of charge transport.

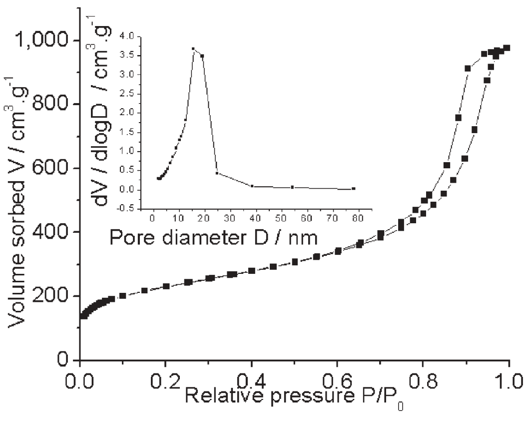

Fig. 4 77 K N_2 sorption measurements. Insert: pore diameter distribution (calculated from the desorption branch of the isotherm using the BJH method).

In conclusion ionogels form a new family of transparent, temperature-resistant solid electrolytes whose preparation and shaping are very easy and cheap. Specifically ionogels could represent a significant advance in electrolyte membranes for fuel cells by working under anhydrous conditions and pushing the limit of the operating temperature from 400 to at least 520 K.[9] This remarkable stability could avoid the current necessity for a drastic control in temperature used to avoid overheating. Above all, operating at higher temperatures should be extremely beneficial for the efficiency of fuel cells, especially by preventing poisoning of the electrolyte by carbon monoxide in direct methanol fuel cells.[1] Moreover numerous applications could be addressed, by tuning the properties of ionogels upon playing with the sol-gel method, with the nature of the sol-gel precursors and with the choice of the ionic liquid. Typically this approach could be extended to mixtures of ionic liquids or to ionic liquids containing additional migrating species (strong acids, lithium salts, iodine, *etc.*).

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Notes and references

† Alternating-current conductivity measurements were carried out with platinum electrodes on a Novocontrol apparatus, with a frequency range from 1 MHz to 10 Hz.

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