Binary inorganic salt mixtures as high conductivity liquid electrolytes for >100 °C fuel cells†

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We report the successful application of low-melting inorganic salts with protonated cations (*e.g.* ammonium) as electrolytes in fuel cells operating in the temperature range 100–200 °C, where even with unoptimized electrodes, cell performance is comparable to that of the phosphoric acid fuel cell operating with optimized electrodes in the same temperature range, while open circuit voltages, and efficiencies at low current densities, can be much better—and there is no need for humidification or pressure to sustain performance.

Over the past two decades there has been a surge of interest in the use of "ionic liquids" as room temperature solvent media of low vapor pressure in which chemical reactions can be carried out without need for control of toxic vapors.[1] Many other useful applications for these media have also been discovered.[2,3] Most recently[4–10] interest has turned to the use of liquids in which the cations are formed by proton transfer, because they tend to be more fluid than the aprotic cases,[8] hence more conductive. In particular, they can also be used as proton transfer media in fuel cells and other electrochemical devices.[6,7,9–11] The possible function of solvent-free ionic liquids as fuel cell electrolytes was first reported by Susan *et al.*,[6] though the use of imidazole and related molecules as proton carriers in polymeric membrane electrolytes had begun in 1998.[12]

In this laboratory we have shown that when ethylammonium nitrate is used as the electrolyte, the cell suffers almost no polarization at the oxygen electrode.[7,9] The result is that the cell voltage closely approaches the theoretical value of 1.15 V at 150 °C. However, we find that the cell lifetime is limited, probably because of C–H bond cleavage in the presence of the platinum catalyst. In the present communication we show that the large organic cation is by no means necessary for the fuel cell electrolyte function. Indeed for purposes of high current density cells, the removal of the organic component seems to bestow an advantage. Here we detail several low melting or low liquidus temperature inorganic ionic liquids and then exemplify their performance in fuel cells by comparing with the performance of the phosphoric acid fuel cell.

Inorganic ionic liquids, in the current sense of ionic compounds that are liquid below 100 °C, are not abundant. Some examples were provided in a recent review.[9] When proton transfer salts are included, the list expands. The low melting points of binary melts containing ammonium salts have long been known to molten salt chemists. The eutectic temperature of 98 °C for $LiNO_3$–NH_4NO_3, for instance, has been known since 1962[13] and its glass temperature was reported in 1971.[14] The inorganic proton transfer salt hydrazinium nitrate, T_m = 70 °C,[15] satisfies the current definition of an "ionic liquid" (melting below 100 °C), and its binary solutions with other hydrazinium salts (and certain ammonium salts also) must have eutectic melting points that are sub-ambient. Because we wish to ensure high temperature stability and to maximize the concentration of proton carriers, we will focus on ammonium salts and their mixtures. The only mention we find of ammonium salts serving as a component of a fuel cell electrolyte is that of Matsui *et al.*[16] where a complex phosphate combination NH_4PO_3–TiP_2O_7 was used at 250 °C. However, the ammonium compound involved is a *meta*phosphate, so the anion is an infinite chain of $[PO_4]$ tetrahedra, and comparison with the simple salts used in our work is hardly appropriate.

Using differential scanning calorimetry to detect the thermal events during heating, we have determined complete phase diagrams for three binary ammonium salt systems ((1) trifluoromethanesulfonate ("triflate", Tf) + trifluoroacetate (TFAc), (2) trifluoroacetate + nitrate, and (3) triflate + nitrate), and find simple eutectic behavior in each case.

The first system has a eutectic temperature of 69 °C, amounting to a freezing point lowering of some 50 °C from the T_m of the lower-melting of the two salts. The second, NH_4TFAc + NH_4NO_3, was expected to have an even lower eutectic temperature but this proves not to be the case. The phase diagram for this system, which proves one of the most suitable for our fuel cell purposes, is shown in Fig. 1. The melting points of a variety of other ammonium salts are listed in Table 1, and eutectic temperatures for some additional pairs are also listed.

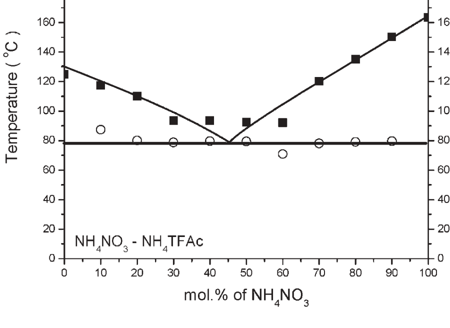

Fig. 1 Phase diagram of the system ammonium nitrate + ammonium trifluoroacetate. The eutectic temperature lies at 79 °C.

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† The HTML version of this article has been enhanced with colour images.

Table 1 Thermal properties of several ammonium salts

Salt and anion formula	T_m/°C	T_e/°C (with…)
Ammonium triflate (Tf) $CF_3SO_3^-$	225	104(NH_4NO_3)
" trifluoroacetate (TFAc) CF_3COO^-	125	69 (NH_4Tf)
Ammonium tetrafluoroborate BF_4^-	230	160 (NH_4Tf)
" methanesulfonate CH_3SO_3-	183	
Ammonium nitrate NO_3^-	169	79(NH_4TFAc)
Ammonium thiocyanate SCN^-	153	72(NH_4TFAc)
Ammonium sulfamate $SO_3NH_2^-$	133	
Ammonium bifluoride HF_2^-	125	
Ammonium hydrogen sulfate HSO_4^-	116	
Ammonium bis(trifluoromethanesulfonyl)imide (TFSI) $(CF_3SO_2)_2N^-$	178	103 (NH_4Tf)
Ammonium bis(perfluoroethanesulfonyl)imide (BETI) $(CF_3CF2SO_2)_2N^-$	237	107 (NH_4Tf)
Hydrazinium nitrate[15]	70	

The conductivities of these melts are very high compared with those of most aprotic ionic liquids. Fig. 2 presents data in the form of an Arrhenius plot where comparison is made with that of ethylammonium nitrate presented in earlier work.[8] At 150 °C the conductivities, many of which reach values of 100 mS cm^{-1}, are comparable to those of aqueous solutions. Included in Fig. 2 are data for two phosphoric acid solutions of different water contents (85 wt% H_3PO_4 closely approximates the stoichiometry $[H_3O^+][H_2PO_4^-]$) which are higher-conducting because of their protonic acid character.

Using in-house Teflon sandwich fuel cells that are described elsewhere,[17] we have determined the current flowing under load when E-TEK electrodes are utilized. Results are shown in Fig. 3. The upper curve shows the remarkably high voltage output of cells using electrolytes containing ethylammonium nitrate EAN, particularly when the EAN is doped with 1% ethylammonium dihydrogen phosphate to reduce its wetting of the E-TEK electrode. Unfortunately, the electrode wetting problem is not really solved and accordingly, these currents are not maintained at high load, relative to those produced by the phosphoric acid cell.

By contrast, in cells using the binary ammonium salts (NH_4Tf + NH_4TFAc) eutectic as electrolyte, the current at high load is maintained in a manner comparable to that of the phosphoric acid cell. However, in this case the open circuit voltage is poor.

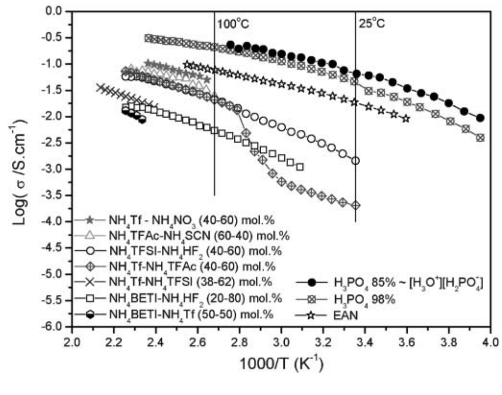

Fig. 2 Arrhenius plot of conductivities of ammonium salt mixtures. Comparison is made with EAN and two phosphoric acids of different water content. High conductivity in solid state is shown for one case.

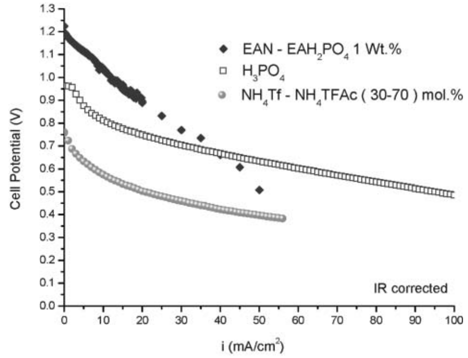

Fig. 3 Total polarization curves for fuel cell with NH_4Tf–NH_4TFAc electrolyte, in comparison with those for phosphoric acid and dihydrogenphosphate-doped ethylammonium nitrate,[17] all measured in the same cell. The curves have been IR corrected. Anode and cathode are ETEK platinum catalyzed porous gas fed electrodes with Pt-loading = 0.5 mg cm^{-2}. Anode feed: hydrogen. Cathode feed: oxygen.

In view of the exceptional voltage output of the ethylammonium nitrate fuel cell, it has been natural to test inorganic electrolytes with ammonium nitrate components. These were subjected to careful pre-tests for explosion potential, and were found to be surprisingly stable, indeed they resisted all attempts to destroy them. The cell using the equimolar NH_4NO_3 + NH_4TFAc electrolyte proves to be the most stable of all electrolytes yet tested, yielding invariant potential at fixed load, day after day of cell use. The cell using 60 : 40 NH_4NO_3 : NH_4Tf yields a very high open circuit voltage, 1.20 V. This exceeds the theoretical voltage 1.15 V

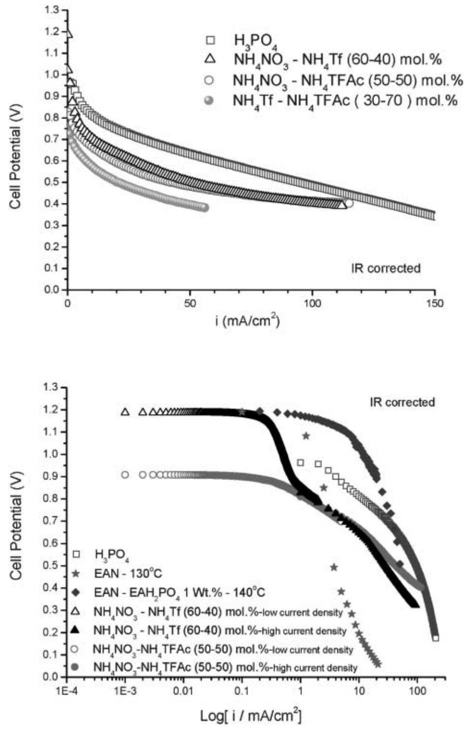

Fig. 4 (a) IR-corrected polarization curves for cells using (1) ethylammonium nitrate, (2) ethylammonium nitrate doped with 1 wt% ethylammonium dihydrogen phosphate, (b) the two inorganic binary salts containing the nitrate anion, shown in the Tafel plot form, cell voltage *vs.* log current density. Overlap of data from independent runs using different current range instruments, establishes reproducibility of behaviour. Plateau implies ideal (barrier-free) reduction at low current.

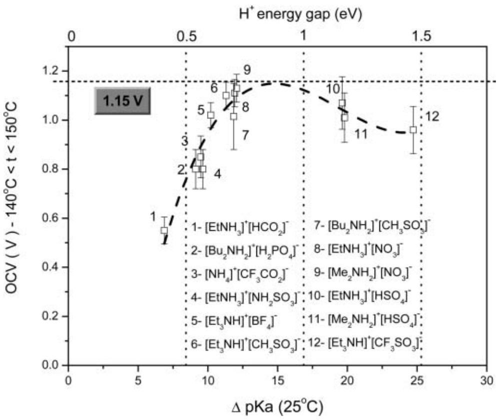

Fig. 5 Open circuit cell voltages in relation to the proton transfer energy gap characterizing the protic ionic liquid electrolyte, showing the range of electrolytes that can yield theoretical fuel cell voltages (see ref. 17 for details).

at 150 °C, due to the low product water activity. Unfortunately, this extraordinary voltage is not maintained under load. These and a number of additional cases are shown in Fig. 4a. The results for selected cases are shown in the Tafel plot form, cell voltage *vs.* log current density, in Fig. 4b. The plateau at 1.20 V in the case of $NH_4Tf–NH_4NO_3$ is particularly striking, signifying ideal barrier-free electroreduction. The reason that the voltage drops abruptly at current densities above 0.5 mA cm^{-2}, but then resumes at a lower cell voltage, must have to do with on-catalyst absorption[18] and will obviously become the focus of future research. A cell that could maintain a 1.1–1.2 V output in the way that the lower voltage outputs of Fig. 4a are maintained, would be an exciting development in fuel cell technology.

Cell voltages in the range 1.15–1.2 V are not confined to nitrate anion-containing ionic liquids. In work being published in detail elsewhere,[17,19] we have shown that this level of open circuit voltage seems to be common to protic ionic liquids that are formed by transfer of protons across a free energy gap of about 0. 6–1.0 eV. To support this assertion, we reproduce from the more detailed publication a key figure showing the relation between measured fuel cell OCV and the proton energy gap between donor acid and acceptor base of the protic electrolyte which, by unproven assumption, is proportional to the aqueous solution metric ΔpK_a. ($\Delta G_{(\text{proton transfer})} = -2.303RT\Delta pK_a$). Conditions under which this assumption can be justified, are discussed elsewhere.[20] A theoretical account of the Fig. 5 correlation is not available at this time. The plot suggests that there will be many protic salts which, used as liquid electrolytes, will yield high fuel cell OCV values.

Finally we should note an additional advantage of the type of fuel cell that this research reveals. Where conventional water-based proton transfer electrolytes (either with water as base, meaning acid electrolytes, or with water as acid, meaning basic electrolytes) are intrinsically corrosive and demand noble metal catalysts, the electrolytes of the present work can be neutral,[20] while still highly conducting and effective as proton carriers. Their benign character not only simplifies cell construction but also opens the door to many alternative catalysts, including heat-stable enzymes, indeed any catalyst that might aid in the oxygen reduction process.

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