Ionic Liquid Redox Catholyte for High Energy Efficiency, Low-Cost Energy Storage

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An approach to energy storage using ionic liquids as joint ion-conducting medium and redox active catholyte material is described. The earth-abundant ferric ion is incorporated as an oxidizing agent in the form of the low-melting NaFeCl₄ in a 1:1 mixture with ethylmethylimidazolium tetrachloraluminate, an ambient temperature ionic liquid. Different possible anode types are considered, and the most obvious one involving liquid sodium (with special wetting of a sodium ion-conducting ceramic separator) is tested. The high voltage >3.2 V predicted for this cell is verified, and its cyclability is confirmed. Operating at 180 °C, an unexpectedly high energy efficiency >96%, is recorded. This establishes this type of cell as an attractive candidate for energy storage. For optimum energy storage, high energy efficiency is mandated for thermal management, as well as economic reasons. The theoretical capacity of the cell is 288 Wh kg⁻¹ (418 Wh L⁻¹) of which 73% is realized. The cell is shown to be fail-safe against internal shorts. As there are many degrees of freedom for developing this type of cell, it is suggested as a promising area of future research effort in the energy storage area.

1. Introduction

Energy storage is widely recognized as one of the key problems in need of solution in our modern society. Green technologies such as wind and solar are currently plunging in cost, but are intermittent and can only fully develop in tandem with energy storage systems that can serve the load-leveling function. Considering the abundance hence low cost, and favorable redox potential of sodium, sodium-based batteries have been widely regarded as a better choice than lithium-ion batteries for large-scale energy storage but others involving multivalent elements such as Ca, Mg, and Al are also possible and would be advantageous in safety (see the Discussion section).

The most familiar sodium-based systems are the liquid sodium batteries such as Na–S and Na–NiCl₂ (ZEBRA),.[1] However, due to the high operating temperatures, >300 °C, needed to maintain good kinetics in the solid electrolyte and solid cathode (NiCl₂) materials, they encounter problems of thermal management and safety, and also impose stringent requirements on the rest of the battery components.

Since the melting point of sodium is only 98 °C, liquid sodium-based batteries may, in principle, operate in the intermediate temperature range, 100–200 °C. The difficulties lie in the less favorable kinetics of solid electrolytes and particularly of solid cathodes. In a recent report,[2] Lu et al. showed that the working temperature of the ZEBRA cell could be lowered to the intermediate range by optimizing the wetting of sodium on the Na–β′–Al₂O₃ separator using a Na–Cs alloy anode. Although their cell cycled well, the quite high (~91%) energy efficiency of the normal ZEBRA battery was lost (decreased to ~81%), presumably because of the intrinsically slow NiCl₂ cathode kinetics discussed in detail by Prakash et al.[3] Indeed, it was this problem with cathode kinetics that inspired us to investigate the liquid phase cathode that we describe in the present article.

Fortunately, various redox couples, such as Fe(II)/Fe(III) and Mn(II)/Mn(III), can be readily incorporated in low-melting ionic liquids, sometimes in very large mole fractions. For instance, we will show that ethylmethylimidazolium chloride (EMICl) forms an ambient temperature liquid with FeCl₃, and that its conductivity is indistinguishable from that of the much-studied EMIMAlCl₄. Like the latter, EMIMFeCl₃ also dissolves large mole fractions of NaAlCl₄ to form liquid EMIMFeCl₃–NaAlCl₄. Again like the latter, the ambient temperature solutions suffer from serious alkali cation trapping effects[5] which, however, can be overcome by raising the temperature to above 100 °C.

Ionic liquids[6] have been much investigated for low-temperature electrochemical and energy applications[7] often because of their wide electrochemical windows and generally favorable safety characteristics (low flammability and vapor pressure for instance). However, despite all the electrolyte activities, the possibility of using ionic liquids as battery cathodes has so far been given little attention. Here, we will demonstrate the favorable properties of the Fe(II)/Fe(III) ionic liquid redox catholyte by combining it with a liquid sodium anode to achieve >96% overall energy efficiency at an intermediate temperature of 180 °C. The working mechanism of this Na–Fe(redox) cell is shown in Scheme 1. We suggest the adoption of ionic liquid redox catholytes as a new direction for low-temperature energy storage research. Furthermore, the particular (alkali metal anode) system that yields this favorable efficiency also yields an open-circuit voltage 3.31 V, which is considerably higher than for either of the two favored liquid alkali metal battery technologies.
To understand our approach, some background is needed. The Fe(II)/Fe(III) couple was first studied in ionic liquids using cyclic voltammetry by the Osteryoung and Hussey groups, and there have been a number of related studies since that time. For example, Tachikawa et al. studied the Fe(II)/Fe(III) couple in ionic liquids doped with different ligands that would preferentially coordinate the transition metal, while Katayama et al. studied this couple in an undoped ethylimidazolium chloride. The latter authors speculated about the possibility of a Na anode battery with this liquid in the cathode, but estimated that the cell voltage would be only about 2 V. While many other redox couples have been characterized in molten salt and ionic liquid media by cyclic voltammetry, to the best of our knowledge no laboratory has actually fabricated batteries to test the energy storage capabilities of redox couple-based catholytes. Our contribution has been to replace the liquid sulfur, and solid NaCl, of the favored technologies with the ionic liquid redox catholyte.

Our interest in cells utilizing redox couple catholytes was stimulated by the observation of important anion basicity effects on redox potentials in ionic liquids. In a recent study of the redox couple Fe(II)/Fe(III) in ionic liquids, it was noted that the potential (referred to Ag/Ag⁺ in a silver-silver chloride cell) could be widely varied, depending on the basicity of the medium in which the redox couple was dissolved. From this study, it was possible to see that a cell in which an appropriate redox couple could be maintained in the liquid state in the cathode half cell, would have a high voltage when coupled to an Na/Na⁺ anode. Given that the potential difference between the Na/Na⁺ and Ag/Ag⁺ potentials in standard aqueous solutions is 3.5 V, Figure 3 of ref. suggests that a sodium–Fe(II)/Fe(III) cell in which the cathode medium is acidic, and of highly Lewis acid character (as in trflate ionic liquids), could have a cell potential of ~3.8 V (comparable to that of the famous Li–LiFePO₄ cell, and for similar reasons).

The solubility of iron triflates in such ionic liquid media is, however, very low, and this would discourage the exploration of oxidic ionic liquid media for redox cathodes. Similar solubility problems limited the attempt of Goodenough and coworkers to use redox couple cathodes in their “new generation” aqueous hybrid alkali metal battery systems. On the other hand, tetrachloroferrates of ionic liquid cations are not only rich in ferric iron but are also low-melting and of exceptional conductivity. While some lowering of the above cell potential must be expected when the near neighbors of the redox-active species are bound chloride ions (as in FeCl₄⁻) rather than bound oxides (as in triflates), the Lewis acid character of FeCl₃ can be expected to provide a good compromise. Thus, we have been encouraged to test the electrochemical possibilities of cells of the class represented by the cell reaction

\[
\text{Na} + \text{Fe(III)} \rightarrow \text{Na}^+ + \text{Fe(II)}
\] (1)

in the ionic liquid medium EMIFeCl₄–NaAlCl₄, at temperatures where the sodium is in the liquid state. Fortunately, like the recently studied system EMIAICl₄–NaAlCl₄, this combination has wide composition domains that are liquid at room temperature. Not surprisingly, also, there are wide composition ranges in the ternary system NaAlCl₄–EMIAICl₄–EMIFeCl₄. This provides for easy manipulation of the cell during assembly and is also important to the performance of our catholyte because it ensures an abundance of available charge carriers (Na⁺) in the catholyte to support the recharging process.

There are many possible versions of this type of catholyte, depending on the initial electrolyte constitution. Two are illustrated in Equations (2) and (3). The essential difference between the two is the production of solid NaCl in Equation (2), compared with its maintenance in the solution in Equation (3)

\[
\text{Na} + \text{EMI}^+ [\text{FeCl}_4^-] \rightarrow \text{EMI}^+ [\text{FeCl}_4^-] + \text{Cl}^{-} + \text{Na}^+ + \text{AlCl}_4^{-}
\] (2)

In applying Equation (2) chemistry, we add additional NaAlCl₄ (or EMIAICl₄ or EMIFeCl₄) to compensate for the higher melting trichloroferrate species that is generated during discharge to maintain the electrolyte in the liquid state (except for the precipitated NaCl). We note that FeCl₃ is not a trigonal anion, but a chain of chloride-bridged tetrahedra, [Fe(II)Cl₄]₃, so this tends to be viscous. A full phase diagram for this ternary system has yet to be generated.

The second case to consider is

\[
\text{Na} + \text{EMI}^+ [\text{Fe}_2\text{Cl}_7^-] \rightarrow \text{EMI}^+ [\text{FeCl}_4^-] + \text{Na}^+ [\text{FeCl}_4^-]
\] (3)

Unless there are additional technical problems to solve (such as Lewis acid attack of cations once the tetrahalometaallate stoichiometry is surpassed) the Equation (3) case should not only have a higher cell potential (due to the increased acidity of the Fe₇Cl₇⁻ anion), but should also have an enhanced capacity (based on Fe as the limiting species). In view of our greater experience with the simple 1:1 class of halometallates, we have explored the Equation (2) case first. The conductivity, electrochemical properties of the [EMIFeCl₄][NaAlCl₄] catholyte, and its application in an assembled Na–Fe(redox) cell are described in the Results section.

2. Results

The conductivities of the several candidate ionic liquids and mixtures are plotted as Arrhenius functions of temperature.

![Diagram of a redox coupling process](image-url)
ingly) the alkali cation-trapping problem in the same oxidation state, which means that (not surprisingly) the alkali salts show the same lower conductivities and larger temperature dependences discussed recently in terms of alkali cation trapping phenomena.\textsuperscript{[3]} Comparison is made with the conductivity of the two common Na ion conducting ceramics, Na mixed and sintered in a controlled temperature oven for testing. With this cell, cyclic voltammograms at 180 °C (Figure 5) were first taken using different scan rates in the range 0.01 to 0.5 V for which no other explanation is obvious. When the potential range is limited to avoid the latter process, the redox process for the Fe(II)/Fe(III) couple is simple and reversible as seen in Figure 2b. The reversibility of the redox catholyte process will be seen to persist in the cell tests and is a major finding of this research.

![Figure 1](image1.png)

**Figure 1.** Specific conductivities of several ionic liquids and their mixtures with Na analogs. Solid symbols are for data taken during heating runs while open symbols are for data taken during the subsequent cooling. For [EMIFeCl\textsubscript{4}][NaAlCl\textsubscript{4}, data from three consecutive runs coincided within measurement uncertainty. The conductivities for this IL superimpose on those for EMIALCl\textsubscript{4} from ref. [5]. The mixtures with alkali salts show the same lower conductivities and larger temperature dependences discussed recently in terms of alkali cation trapping phenomena.\textsuperscript{[3]} Comparison is made with the conductivity of the two common sodium ion conducting ceramics, Na mixed and sintered β’-β” alumina, and NaSICON.

![Figure 2](image2.png)

**Figure 2.** Cyclic voltammograms of [EMIFeCl\textsubscript{4}][NaAlCl\textsubscript{4}, catholyte for different voltage ranges, a) −1.3−1.3 V, b) −0.4−0.05 V, Pt as reference electrode, scan rate 10 mV s\textsuperscript{−1}, T = 180 °C. Processes associated with different peaks, or displacements, are indicated on the plots. The third oxidation peak at 0.5 V for which no other explanation is obvious. When the potential range is limited to avoid the latter process, the redox process for the Fe(II)/Fe(III) couple is simple and reversible as seen in Figure 2b. The reversibility of the redox catholyte process will be seen to persist in the cell tests and is a major finding of this research.

In order to evaluate the performance of the redox catholyte in a full cell, a cell using liquid sodium as the anode and NaSICON as a single ion conducting separator was assembled. As shown in Figure 3, it is a planar design utilizing flat viton gaskets to seal the anode and cathode chambers. Because the problems of ceramic wetting by liquid alkali metal are well known,\textsuperscript{[3]} we used a light sputtering of indium–tin oxide (ITO) to reduce the surface tension and allow spreading of the sodium anode during an initial exposure of the anode compartment to 300 °C. The contact angle changes induced by temperature change are shown in Figure 4, where it is seen that the controlled spreading induced at 300 °C is maintained on lowering of temperature. The anode and cathode compartments were then joined and sealed, via insulated bolts and a second viton gasket, and the unit mounted in a controlled temperature oven for testing.

With this cell, cyclic voltammograms at 180 °C (Figure 5) were first taken using different scan rates in the range 0.01 to 0.5 V for which no other explanation is obvious. When the potential range is limited to avoid the latter process, the redox process for the Fe(II)/Fe(III) couple is simple and reversible as seen in Figure 2b. The reversibility of the redox catholyte process will be seen to persist in the cell tests and is a major finding of this research.
0.20 mV s\(^{-1}\). At the lowest scan rate we used, 0.01 mV s\(^{-1}\), the peak-to-peak separation is \(E_{pa} - E_{pc} = 70\) mV, slightly larger than 59 mV (the ideal reversible value) and the difference becomes larger (170 mV at the maximum scan rate, 0.20 mV s\(^{-1}\)), indicating that the redox process for Fe(II)/Fe(III) in the ionic liquid medium contains a kinetic component (usually diffusional) that causes a hysteresis between the reduction (\(E_{pc}\)) and oxidation peak (\(E_{pa}\)) potentials. However, the integrated areas of cathodic and anodic scans are almost the same, indicating a very high coulombic efficiency (reversibility of the charge–discharge process).

At slow rates there are two steps in the redox process. The origin of the split is not known, but a reasonable surmise is that it is a manifestation of the Marcus theory for the total electron transfer process as follows. Considering the discharge process, stage 1 would be electron transfer to Fe(III)Cl\(_4\)^\(-\) to produce transiently (Fe(II)Cl\(_4\)^2\(^-\)) followed by stage 2, the reorganization of the structure from single tetrahedral anions (Fe(II)Cl\(_4\)^2\(^-\)) to corner-linked tetrahedral chains of formula FeCl\(_3\)^\-. That the solvent reorganization is a significant part of the free energy change in most electron transfer processes (Marcus theory) and the chain structure for ions such as FeCl\(_3\)^- is known from old Raman studies on the analog system KCl–ZnCl\(_2\).

At higher rates, the major process begins at the same potential during oxidation as it is does during reduction, implying a high order of reversibility in this process. The cell voltage, 3.25 ± 0.05 V, taken from these onset points, is considerably higher than those of the common “liquid sodium” batteries, Na–S (2.0 V) or Na–NiCl\(_2\) (2.58 V), as anticipated from the considerations outlined in the Introduction. The redox process takes place between 3.0 and 3.5 V, so the Na–Fe(redox) battery can be charged and discharged within this range.

Most important, of course, and also most promising, is the cell performance in its charge and discharge functions, which was tested according to the following protocol. As is commonly recommended, the cell was conditioned by an initial charge/discharge cycle conducted at very slow rates, 0.02 C over 10 h where...
Figure 6. a) Charge/discharge curves for different cycles of the Na–Fe(redox) battery at 180 °C, the discharge rate is 0.1 C, and the charge rate is 0.05 C. After the cycling, a conditioning process has been done by charging/discharging at a low rate of 0.02 C for 10 h. b) Coulombic, voltage, and energy efficiencies as a function of cycle number.

C has its usual meaning. (The charge and discharge current is measured in C-rate. A discharge of 1 C draws a current equal to the rated capacity. For example, a battery rated at 1 Ah provides 1 A for 1 h if discharged at 1 C rate.) Following such conditioning, the cell was cycled using a slower charge rate (0.05 C) than discharge rate (0.1 C) because of the need to redissolve the precipitated NaCl during the charging cycle. Such asymmetric kinetics are also seen in the cases of Na–S and Na–NiCl₂ cells.

After conditioning, the voltage versus capacity behavior was studied, and the results are shown in Figure 6a. Apart from the capacity fade (~1% per cycle), the results are remarkable. The charge and discharge voltage profiles are nearly symmetrical (as expected from the CV test of Figure 5) and the average coulombic efficiency is 98.2%, indicating that sodium ion transport across the NASICON is essentially reversible and there are almost no side reactions during the charge and discharge processes. The coulombic efficiency in the first cycle is 102% and then decreases to 98% in the following cycles. The anomalous coulombic efficiency in the first cycle might be caused by some impurity, which can be reduced in the discharge process. The charge voltage plateau is around 3.31 V and the discharge voltage plateau is around 3.25 V. There is only 0.06 V difference between charge and discharge processes at midpoint, which also demonstrates the high degree of reversibility. The polarization becomes gradually larger with the cycle number, leading to the slow decrease of voltage efficiency seen in Figure 6b.

The cell capacities, expressed in mAh g⁻¹, will depend on the composition of the catholyte that is needed (i) to maintain the liquidus temperatures below operating temperatures and (ii) to optimize conductivities. For the choice made in the cell reported herein, the electrolyte had the simple molar composition EMICl, FeCl₃, NaCl, and AlCl₃ in mole ratio 1:1:1:1, which is the same as [EMIFeCl₃]₀.₅[NaAlCl₄]₀.₅. Based on the cathode active component EMIFeCl₃, we can calculate its theoretical capacity to be 87.0 mAh g⁻¹. Given the open-circuit voltage (OCV) of 3.31 V and the liquid density of 1.45 g mL⁻¹, the theoretical energy densities are 288 Wh kg⁻¹ and 418 Wh L⁻¹. In light of experience, this is not the optimum composition for our electrolyte for full Fe(III) to Fe(II) reduction. The compositions with higher theoretical capacity and conductivity are the subject of ongoing investigation.

The capacity we get in the first cycle of Figure 6a is 64.5 mAh g⁻¹, which is 73% of the theoretical capacity. While the cell cycles well near its reversible potential, there is clearly a source of capacity loss (23% after 20 cycles) to be overcome. The source of the loss is possibly associated with slow redissolution of precipitated NaCl, or of the higher melting product EMIFeCl₃ (that could be ameliorated by including extra EMIFeCl₃ in the catholyte). However, it might equally be related to a residual sodium wetting problem, for which the Na–Cs alloy technology described by Lu et al. might provide a solution. Our initial battery design is likely also to be the source of some performance problems.

We note that a cell based on the Equation (3) chemistry would avoid any NaCl precipitation–redissolution problem, but this process will likely require an electrolyte with lower FeCl₃ activity, such as those based on partly oxygenated cathols (as described by Xu et al.) to avoid further parasitic Fe²⁺ reduction.

While the above problems will be addressed in future work, the important achievement of the present work is not so much the performance of an alkali metal-based cell as it is our demonstrated possibility of the very high energy (storage/recovery) efficiencies that can be obtained using this liquid redox catholyte. The energy efficiency is calculated according to the following equation (where \( V_{mid} \) is the voltage value at 50% depth of charge or discharge, based on successive charge–discharge cycles. For the present results, it is 96.2%)

\[
\text{Energy efficiency} = \frac{\int V_{\text{discharge}} \cdot i_{\text{discharge}} \, dt}{\int V_{\text{charge}} \cdot i_{\text{charge}} \, dt} = \frac{V_{\text{mid}} \cdot \text{discharge} \cdot C_{\text{discharge}}}{V_{\text{mid}} \cdot \text{charge} \cdot C_{\text{charge}}}
\]

\[
\approx \frac{\text{voltage efficiency}}{\text{coulombic efficiency}}
\]

The data on which the calculation is based, for each successive cycle, are shown in Figure 6b. The energy efficiency is related to, but must always be smaller than, the coulombic efficiency, which is also shown in Figure 6b. We emphasize that neither coulombic efficiency nor energy efficiency shows a very
adverse trend with a cycle number. It is common for energy efficiency to be considerably lower than coulombic efficiency, and to have different causes. Energy inefficiency is usually due to irreversible aspects of the electrode processes rather than to side reactions. For energy storage purposes, high energy efficiency is of central importance.

3. Discussion

Although our emphasis has been primarily on the advantages of the liquid redox catholytes described herein, it must be recognized that their exploitation for energy storage purposes is most likely to involve a combination with alkali metal anodes in one form or another (though combination with multivalent metals such as magnesium and aluminum is an option for future study, see below).

Safety is then a matter of primary importance. In the case of failure of the solid ceramic separator, the anode material can make direct contact with the catholyte, with release of the stored energy an obvious matter of concern. We first note that the direct reactions between the anodic active material (molten metallic sodium) and the catholyte (EMIFeCl₄–NaAlCl₄) lead to solid, or unreactive liquid, not gaseous, products, according to the following equations

\[ 3Na + EMIFeCl₄ \rightarrow EMICl + 3NaCl + Fe \]  
\[ 3Na + NaAlCl₄ \rightarrow 4NaCl + Al \]  

Since no gases are produced there is no potential for explosion unless the heat of reaction is instantly released. The potential for hazard by direct contact of liquid sodium and catholyte was tested by pouring the active catholyte liquid directly onto shiny molten sodium in a container in a low pO₂ dry box (see the video in the Supporting Information), and the total absence of any hazardous response has been the unspectacular result. The sodium is slowly blackened as it reduces the metal ions in the catholyte. Evidently, the fire hazard from internal shorts in this system is minimal.

The other practical consideration is the materials cost. These account for 78%–80% of total cell cost for batteries manufactured in large volume by automated equipment according to Brod's report. The Na–Fe(redox) battery should have a low cost since the elements involved, Na, Fe, and Al, are cheaper than traditional battery materials such as Li, Co, and Ni. This is why sodium anode based cells are favored for large-scale energy storage, and why the LiFePO₄ cathode is popular for electrical vehicle power trains. In addition, NaSICON is considerably less expensive than β-alumina according to a Ceramatec report.

The combination of these considerations with the energy efficiency advantage emphasized in the previous section provides a powerful motivation for further exploration of the redox catholyte strategy for medium temperature electrochemical energy storage purposes.

To add substance to the latter issue, we contrast our energy efficiency finding of >96.0% with the lower values (~81%) evident in ref.[2] for the ZEBRA cell running at the same intermediate temperature, and with those that can be found in the literature. The classic case of the lead acid battery, for instance, is illustrated by the charge/discharge voltage curves that may be seen in various sources, e.g., ref. [20]. Assuming 100% coulombic efficiency, the mid-voltage gap would indicate an energy efficiency of only ≈87%, which is typical of various commercial systems. Divya and Ostergaard [21] listed the following assessments for energy efficiency of leading battery systems: Na–S (89%), lead acid (72%–78%), NiCd (72%–78%), vanadium redox (85%), zinc–bromine (75%), metal–air (50%), and regenerative fuel cell (75%). High voltage efficiency, leading to high energy efficiency (about 90%), was also a feature of the aqueous hybrid redox battery [23] (of which our ionic liquid battery is a safer relative), but it was accompanied by low capacity due to low redox couple solubility. Only the lithium-ion battery achieves the desired ≈100% with acceptable capacity. Our cell, even at this early stage of its development, approaches the latter performance. It is unlikely that, in our initial studies, we have chosen the optimum electrolyte composition within the ternary system, and it is certain that we have not developed the optimum cell design, so better results can be expected in future work.

Concerning alternative and safer anodes using multivalent metals, the most obvious is the aluminum anode. In this case, the solid aluminum is maintained in a bath of a similar ionic liquid to that used in the cathode, but contains only chloroaluminate anions at sufficient acidity for facile Al deposition. Additional Al³⁺ ions generated in the discharge cause Na⁺ ions from the bath to migrate to the cathode compartment, and the cell reaction is then completed as in the Na anode case we have described. This development will be the subject of subsequent reports.

We should emphasize the number of degrees of freedom available within the liquid redox catholyte field for future development. The Mn(II)/Mn(III) couple is an obvious case to explore for higher voltages, whereas multielectron transfer couples such as Cr(III)/Cr(VI) (or the less toxic molybdate analog), which are reversible both in aqueous acid systems and in high-temperature oxidic solvents [24] remain to be explored.

Here we would note again that the catholyte, when correctly formulated, is an ambient temperature, freely flowing liquid. It is not difficult, then, to imagine its potential to serve in a flow battery system, and even in a “gas station” facility in which the spent catholyte is drained out, and replaced with a fully oxidized catholyte of low sodium content (since Na⁺ ions are generated on discharge). This would require the system to carry excess sodium metal, and the number of such “quick recharges” would be limited by this sodium supply. Replenishment of the sodium supply could only be accomplished by a normal electrochemical recharging process.

4. Conclusions

We have demonstrated that the known high energy efficiency of (solid cathode) lithium batteries, relative to those of other commercial systems, can be obtained using liquid cathodes, without sacrifice of high cell voltages. Because high efficiency is mandatory for large-scale energy storage and because liquid cathodes have great compositional flexibility and can use more earth-abundant materials, the new approach we have described deserves further development.
This work also illustrates a new direction for application of ionic liquids, whose primary disadvantage of low conductivity at ambient temperatures can be overcome by operating at moderate temperatures. There are many possibilities for increasing the energy capacity of this type of catholyte.

While we have successfully used liquid sodium as one example of a compatible anode, we can recognize many other anodes that will be compatible with the same or similar cathode technology. It is important that the technology has been shown fail-safe against internal shorts in the case of liquid sodium anodes.

Improvements in separator technology and cell design are needed to further improve the performance of the cell described in this work.

5. Experimental Section

Materials and Catholyte Preparation: Anhydrous 1-ethyl-3-methylimidazolium chloride (EMICl), FeCl$_3$, AlCl$_3$, and NaCl were all purchased from Sigma-Aldrich. NASICON was supplied by Ceramatec company. All materials were stored and used in an argon atmosphere glovebox. The preparation of the anhydrous catholyte was very simple, just by mixing the anhydrous EMICl, FeCl$_3$, NaCl, and AlCl$_3$ by a molar ratio of 1:1:1:1 (the optimum molar ratio of EMICl, NaCl, and AlCl$_3$ was the subject of ongoing investigation). EMICl and FeCl$_3$, spontaneously fused to an ambient temperature liquid. The AlCl$_3$ and NaCl then added were slower to dissolve but yielded a homogeneous solution after heating at ≈200 °C for about 30 min.

If the temperature was raised above 160 °C on unprotected samples, the color of the melt darkens probably due to the effect of temperature on the Fe–Cl charge transfer band. However, the cell performance seemed unaffected up to 200 °C. Control of AlCl$_3$ activity by the buffering strategies of Koronaios and Osteryoung could be useful to control the temperature range of the battery.

Electrochemical Characterization:

Conductivity Determinations: Conductivities of transition metal-containing ionic liquid electrolytes of interest were surveyed using twin Pt wire dip-dip electrodes sealed into stainless-steel threaded caps that were screwed onto glass vials containing the samples loaded under nitrogen in a drybox. The sealed cells were weighed before and after measurements to check on sample integrity during the study. Data were taken using a PAR VMP2 potentiostat (Princeton Applied Research) in the frequency range 10–100 kHz during slow heating from ambient to 200 °C and also during cooling to confirm that ramp rates were slow enough to yield equilibrium data and to ensure that no sample decomposition or crystallization occurred in the temperature range of study. Frequency-independent conductivity values were obtained from the Nyquist plots following the precautions discussed by Tucker and Angell [2].

Cyclic Voltammetry: The electrochemical properties of the catholyte were investigated by cyclic voltammetry (CV) using a potentiostat/galvanostat (Princeton Applied Research, VMP2). A three-electrode cell was employed with platinum as the working, and counter electrodes, as well as the reference electrode. All the scans were made at 180 °C at a scan rate of 10 mV s$^{-1}$.

Demountable Battery Design and Assembly: The assembled cell is shown in Figure 3a, and the cell scheme is shown in Figure 3b. For machining convenience, the cathode compartment was made from stainless steel, but this needed protection from reaction with the Fe(III) of the catholyte. For our present testing this was achieved with a platinum foil. A next-generation version would use a quite different design with ceramic casing, stress-free separator, and upper copper cap with seal. While it was the practice in ZEBRA battery practice to generate liquid sodium in the anode section in situ during charging, it was alternatively chosen to introduce sodium metal into the anode section in an initial stage to take advantage of a ceramic-wetting procedure that was found to give better anode performance for the early stage of battery development. Copper wool was pressed into a pellet (350 mg, density 1.75 g cm$^{-3}$) to fill in the cathode chamber and used as the current collector; the open structure also allowed for sodium volume expansion and contraction during operation. Carbon felt (3 mg, density 0.08 g cm$^{-3}$) was used as the current collector for the catholyte, and about 50 mg liquid [EMIFeCl$_6$][AlNaCl$_4$]$_{0.5}$ was absorbed in the carbon felt. It also provided a wicking effect that ensured effective catholyte contact with the NaSICON separator.

ITO Coating and Wettability Testing: Without the ITO coating, it was found that the battery could not be reversibly charged and discharged at 140 °C, because of the poor wetting of the liquid sodium on the ceramic disk. Concerning the thickness of the ITO coating, it was noted that the sputtering was designed for minimal and discontinuous coverage, so thickness was not a good parameter. An average of island heights would be 5 nm based on amount of ITO sputtered (not all reached the target). A sessile drop technique was used to test the wettability of NaSICON of sodium, with and without ITO coating. Complete wetting of the liquid on a solid surface meant that the contact angle was zero or close to zero such that the liquid spread over the surface easily. Contact angles greater than 90° allowed the liquid to ball up when it can easily run off the surface. Solid sodium pieces were placed on the NaSICON disc heated on a hot plate in a glove box with low H$_2$O and O$_2$ (<0.1 ppm), and the temperature raised and lowered in the sequence indicated in Figure 4.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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