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Stability of Sodium Couple in Organic and Inorganic Molten Salt Electrolytes Investigated with Electrochemical Quartz Crystal Microbalance

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An electrochemical quartz crystal microbalance (EQCM) was used to examine the sodium plating-stripping reactions in two room-temperature molten salts: (*i*) buffered-neutral 1-methyl-3-propylimidazolium chloride and (*ii*) methanesulfonyl-aluminum chloride. In cyclic voltammetry scans on melt (*i*), slightly more mass was plated on the electrode than required by the charge passed for sodium reduction. The excess mass deposition suggests coreduction of either electrolytes or impurities and formation of protective layers; this results in irreversible deposition and less than 100% coulombic efficiency. In chronoamperometry scans, the mass deposition rate was lower than the equivalent charge passed for pure sodium. This indicates possible reaction between sodium metal and the electrolytes or impurities at the electrode surface after depletion of sodium ions. The inorganic molten salt melts, (*ii*), were made of aluminum chloride, methanesulfonyl chloride, and sodium chloride. The amount of sodium chloride added to melts was critical to the stability of the sodium deposited. The highest coulombic efficiency for the sodium couple in these melts was 97%, and the self-discharge rate was 3 μA/cm^2. The EQCM results showed reduction of the electrolyte or reaction with sodium metal forming irreversible products.
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The need for low-cost, dependable, high-energy density, rechargeable batteries continues to escalate with the demands of the electronics and automobile industries. Use of a sodium-metal anode has been studied as an alternative to the lithium-based battery due to some potential advantages. Formation of lithium dendrites during deposition has required the use of a separator and lowered the coulombic efficiency.[1,2] A wide separation of these electrodes could result in high resistance and low current density. Sodium-anode batteries, in contrast, can be constructed with a minimum of free electrolyte between electrodes; sodium deposits evenly on the surface of the electrode. Furthermore, the supply of sodium is essentially infinite; these two factors may make sodium an attractive anode alternative.

The use of sodium at or near room temperature demands an electrolyte that is low-melting, ionically conductive, with a broad enough electrochemical window to permit both the deposition of sodium and a corresponding cathode reaction. Most of the past work has focused on organic-based electrolytes consisting of aluminum chloride, an organic salt, and a Lewis acid, in which is dissolved a sodium salt.[3,4] For example, the buffered neutral 1-ethyl-3-methylimidazolium chloride melts are made of aluminum chloride, 1-ethyl-3-methylimidazolium chloride (EMIC), sodium chloride, and hydrochloric acid (HCl).

Preparation of these electrolytes starts with ''acidic'' melts, made by mixing more aluminum chloride than EMIC ($N = 0.55$, where N is the mole fraction of the aluminum chloride). Excess aluminum chloride results in a Lewis acidic melt. The acid form of aluminum chloride in the melt is $Al_2Cl_7^-$. Sodium chloride (a Lewis base) is then added, neutralizing the acidic melt by reacting with Lewis acid species, and producing the neutral species, $AlCl_4^-$. This buffered-neutral EMIC melt has a wide electrochemical window, 47 V, and a high conductivity, 0.035 S/cm.[4-7] Despite the wide electrochemical window, its negative limit lies close to the reduction potential of sodium ions. EMI^+ cations may be electrochemically reduced, possibly forming neutral radicals. Adding a small amount of a Lewis acid facilitates the electrochemical reduction of sodium ions to sodium metal.[4] Thionyl chloride has been used as the additive in place of HCl and allowed good coulombic efficiency for sodium reduction/oxidation. However, dark-colored films were observed on the working electrode after plating sodium in these types of melts. These were believed to be the reduction products (mixture of sodium and melt) or simply the reduced melt itself. There was also a proposition that these are solid electrolyte interfaces (SEIs). This is still under investigation.[7,8] Formation of these films is irreversible and lowers the coulombic efficiency of the sodium redox couple in the organic melts.[4,7]

Angell and others proposed molten salt electrolytes with an inorganic liquid salt replacing the organic salts. The cathodic limit of many of these melts was 1 V negative of the sodium redox couple.[9] The most attractive of these inorganic electrolytes was made from methanesulfonyl chloride, aluminum chloride, and a sodium salt ($N = 0.5$). The coulombic efficiency recorded for sodium or lithium couples in these electrolytes previously was between 50 and 90%, and the conductivity was $10^{-4.5}$ S/cm at 25°C. The higher efficiency was only observed at slow scan rates, *ca.* 1.0 mV/s, and is probably due to formation of a passivating film on the working electrode. The source of the efficiency loss (less than unity coulombic efficiency) was unknown.[9]

In this paper, an electrochemical quartz crystal microbalance (EQCM) was used to investigate the loss of coulombic efficiency for the imidazolium melt and the methanesulfonyl chloride melt. In particular, the potential (and current) where the coulombic efficiency is less than unity is important in understanding the mechanism of the parasitic reaction. The EQCM can be used in controlled potential or current electrochemical experiments. The mass can be obtained from the Sauersbrey equation[10-14]

$$\Delta f = -\frac{2f_0^2 \Delta m}{A(\mu_q \rho_q)^{1/2}}$$

where Δf is the frequency shift, f_0 is the resonant frequency, Δm is the mass change, A is the piezoelectrically active area, μ_q is the shear modulus of the quartz crystal, and ρ_q is the density of the quartz crystal. The mass change of the quartz crystal is inversely proportional to frequency shift. Linearity of frequency change with respect to mass change was observed from this relationship up to certain thickness of the deposition film.[11,12] Mass change can be related to charge passed according to Faraday's law

$$\Delta m = \Delta Q \frac{(MW)}{nF}$$

where MW is the molecular weight, n is the number of equivalents per mole, and F is the Faraday constant.[11]

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Table I. Composition of the melts used.

Name	Mole fraction of $AlCl_3$	Mole fraction of salt	NaCl added (mol/kg)	Lewis acid (μL/mL of melt)
Melt A	0.55	0.45 MPIC	2.1	400
Melt B	0.50	0.50 MSC	1.9	None
Melt C	0.35	0.65 MSC	2.5	None
Melt D	0.27	0.73 MSC	1.9	None

Experimental

Aluminum chloride was obtained from Aldrich Chemical (Milwaukee, WI) and purified as described previously.[3] Methanesulfonyl chloride was 99% pure, Aldrich Chemical, and vacuum dried using phosphorous pentaoxide.[15] Sodium chloride (99.999%) was obtained from Aldrich Chemical and used as received. 1-methyl-3-propyl imidazolium chloride (MPIC) was prepared by reacting 1-methylimidazole with propyl chloride, both Aldrich Chemical, followed by crystallization and further purification, as described previously.[4] Thionyl chloride (Aldrich Chemical) was used as received.

EG&G model 273 and 263 potentiostats were used for cyclic voltammetry (CV) and chronoamperometry (CA). The electrodes were fabricated from 0.5 mm diam, 99.9999% pure, aluminum wire (Alfa Metals, Ashland, OR) and 99.999% pure platinum wire (ESPI, Ward Hill, MA). The working electrode was a platinum or aluminum disk and the counter electrode was platinum. The reference electrode was formed by immersing an aluminum wire in the acidic EMIC melt (0.4 mole fraction of ethyl methyl imidazolium chloride and 0.6 mole fraction of aluminum chloride) in a glass tube separated from the main melt by a glass frit.[4] The mole fraction of aluminum chloride is designated as N throughout the text. The conductivity of the melts was measured using a calibrated conductivity meter and a 1.0 cm diam tube fitted with platinum electrodes. The melts were prepared in a nitrogen-filled dry box (Vacuum Atmospheres Co., Hawthorne, CA) operated with the oxygen and water concentrations below 10 ppm.

An EQCM (EQCN-701) from Echema (New York, NY) was used in the melts to measure the mass of the electrodeposited sodium. The working electrode in the EQCM experiments was a 10 MHz AT-cut platinum-coated quartz crystal (ICM, Oklahoma City, OK). The EQCM cell was operated in a Faraday cage to minimize electrical noise. A Pine Instruments potentiostat model 366 was used with an EG&G 175 universal programmer and an HP 7090A plotter.

Two types of room-temperature molten salt electrolytes were used in this study and will be referred to by letter designation. The previously reported MPIC melt was used in the buffered neutral form (melt A). The acidic form of melt A was first prepared by mixing MPIC with aluminum chloride ($N = 0.55$), followed by neutralization with a twofold excess of sodium chloride. The resulting melt was Lewis neutral and buffered with the excess sodium chloride. Lastly, thionyl chloride (Lewis acid) was added to enable the electrodeposition of sodium metal.[4]

The methanesulfonyl chloride melts were prepared by adding small increments of aluminum chloride to methanesulfonyl chloride (MSC). The equimolar MSC electrolyte, melt B, was heated during preparation because of the low saturation limit of aluminum chloride in MSC. A second MSC electrolyte, melt C, was prepared by mixing 65 mol % methanesulfonyl chloride with 35 mol % aluminum chloride ($N = 0.35$). The $N = 0.35$ melt (melt C) was usable at room temperature because of the adequate solubility of aluminum chloride. Excess sodium chloride was added to each MSC melt prior to use. Table I lists the composition of each melt.

The EQCM was calibrated for charge-to-mass deposited by electroplating copper from an acidic, aqueous copper sulfate solution. A duplicate calibration was also performed by depositing silver from an acidic silver nitrate solution. The potential of the quartz crystal electrode was cycled to values negative of the deposition potential and the mass change and charge were recorded. The potential of the quartz crystal working electrode was scanned positive of the deposition potential and the metal was stripped from the surface. The recorded mass returned to the original, preplating value.

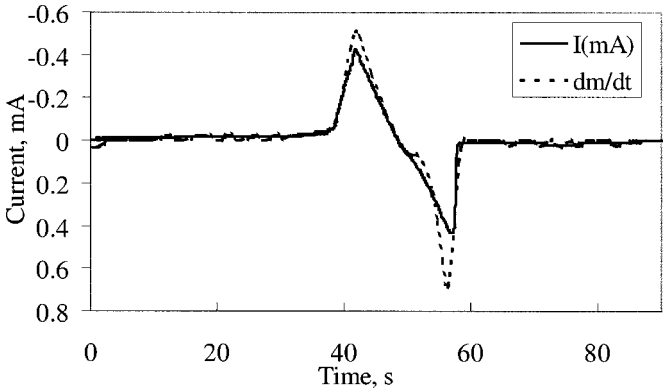

Figure 1. Cyclic voltammogram ($v = 50$ mV/s) on platinum for the buffered-neutral MPIC melt (melt A). Working electrode area 0.196 cm^2.

Results

The electrodeposition/stripping of sodium from a room-temperature MPIC melt occurs at less than unity coulombic efficiency.[4] The coulombic efficiency is defined as the number of coulombs observed during oxidation of the sodium per coulomb expended during reduction of sodium ions to sodium metal. If coulombic efficiency is 1, then the charge stored in the form of sodium metal (negative battery electrode or anode) would be fully recoverable. An efficiency of less than unity could be a result of an electrochemical side reaction, such as from the reduction of an impurity or reduction of the electrolyte itself. A quantum efficiency less than one could also result from the spontaneous reaction of the deposited sodium with either the electrolyte or impurities in the electrolyte. Obviously, the sustained, spontaneous consumption of the sodium from the electrode results in the self-discharge of the anode. In previous studies, the coulombic efficiency of the sodium electrode was measured in melt A (buffered, neutral MPIC melt) and it was found that self-discharge of the electrode occurred. The origin and nature of the self-discharge reaction was not identified. The potentials at which loss of coulombic efficiency and deviation from expected mass changes occurred (assuming the electroreduction of sodium ions to sodium metal) are important to understanding the nature of the parasitic reactions.

The current-voltage behavior and change in mass for an EQCM working electrode in MPIC melt (melt A) is shown in the cyclic voltammogram in Fig. 1 (current is the solid line). The voltammogram is shown as a function of time to avoid overlap of the curves after potential reversal. The scan rate was 50 mV/s and electrodeposition of sodium was observed at potentials negative of -2.4 V. Thus, the time from onset of plating at -2.4 to -2.6 V (the switching potential) at the negative limit is 4 s. The time back to zero current, from -2.6 to -2.2 V, is 8 s. At potentials positive of -2.2 V (on the return scan), the stripping of sodium can be seen. In Fig. 1, stripping occurred from -2.2 to -1.76 V. The coulombic efficiency, ratio of the anodic to cathodic charge in Fig. 1, was 77%.

Superimposed on the graph in Fig. 1 is the result from the EQCM, shown as the dashed line. The time derivative of mass (dm/dt multiplied by Faraday's constant and divided by the atomic weight of sodium: 22.99) is plotted in milliamperes, the same units as the solid current line. Thus, if all the current were being utilized exclusively in the plating and stripping of sodium, the dashed line would exactly trace the solid line. The mass efficiency, the area of negative mass change divided by positive, is 83%. During the plat-

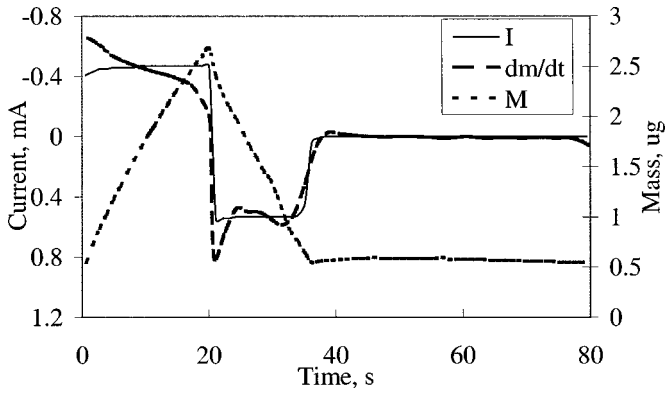

Figure 2. Chronoamperogram on platinum for the buffered-neutral MPIC melt. Reduction was at −2.6 V for 20 s. Oxidation was at −1.85 V for 60 s. Electrode area 0.196 cm^2.

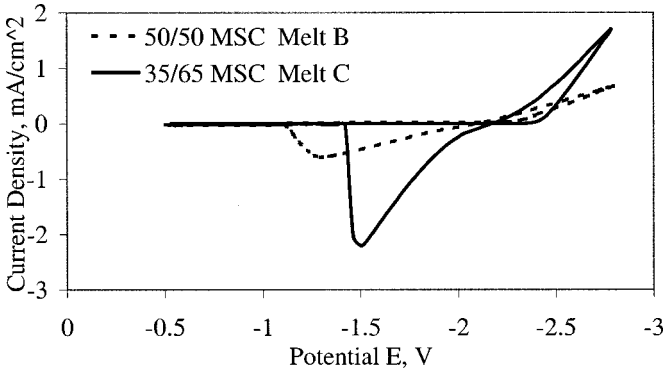

Figure 3. CV (v = 100 mV/s) on platinum for the 50/50 MSC melt (melt B) and the 35/65 MSC melt (melt C).

ing portion of Fig. 1, there is 5% more mass deposited on the electrode than expected from pure sodium. On stripping, 83% of the total mass plated is removed.

These results coincide with those of Gray and co-workers,[4] who, from their voltammetry results alone, speculated that the less than 100% coulombic efficiency was mainly due to reaction of plated sodium with electrolyte. Here the extra mass on plating may be due to some reactions and precipitation of the electrolyte, some of which may remain on the electrode. If the 1-methyl-3-propyl imidazolium cation were reduced resulting in precipitation, then the mass increase on the EQCM would be greater than that observed for the reduction of sodium ions due to the higher molecular weight for the imidazolium product than sodium. It was also possible that electrolyte was reacting with plated sodium and resulting a protective layer on the sodium.[8] Previous studies have shown that the reduction product of an imidazolium chloride melt (1-ethyl-3-methyl imidazolium chloride) was electroinactive and not a dimer.[16] On stripping, the sodium remaining on the electrode is oxidized and lowers the mass on the quartz crystal. However, the mass decreases faster than that expected from a sodium-only process. This is most likely due to insoluble products formed by reduction of the melt (either directly or via the reaction of sodium with the melt) that fall off the electrode as the sodium is oxidized. There is a small fraction (17%) of the mass deposited on the electrode which remains on the quartz crystal. Visually this was seen as a dull film and was difficult to remove by cleaning with solvent. It is most likely a reduction product of the melt or protective layer. Further analysis on this film is in progress.

Figure 2 shows the results of a chronoamperogram using the EQCM in melt A. The voltage was held at −2.6 V *vs.* the Al reference for 20 s during which time sodium was plated. After 20 s at −2.6 V, the voltage was stepped to −1.85 V for 60 s during which time the sodium is oxidized. The current, mass, and time derivative of the mass in units of milliamperes are plotted. Early in the plating step (first 10 s), more mass is added to the electrode than would be expected from pure sodium, as indicated by the difference between the dashed (dm/dt) and solid (current) lines. This is similar to the additional mass seen in Fig. 1 at the most negative potentials during its plating phase. It is potentially due to the protective layer on the sodium as plated or coreduction of electrolyte. Later in the plating step (between 10 and 20 s into the plating experiment), the current and dm/dt curves cross, indicating that the rate of mass increase is now less than that expected from a sodium-only reduction process. This may be due to either a depletion of the reactant (sodium ions) at the electrode surface and reduction of a second species or failure of the solid product to adhere to the electrode surface. Another possible explanation is that the protective layer was dissolved as the concentration of sodium ion drops, and the electrodeposition rate of sodium was less than the dissolution of the protective layer. On stripping, 97% of the total mass plated was removed, but not all of this mass is sodium because the coulombic efficiency was only 86%. The higher mass loss during the initial seconds of oxidation are similar to those seen in Fig. 1. The improved coulombic efficiency, over that observed in the voltammetry, is due to the longer time at the negative voltage limit; more of the negative current has resulted in sodium plating. Likewise, in the stripping step, more of the positive current is used to oxidize the sodium. Some of the plated sodium is again lost to reaction with the electrolyte, in agreement with the results of Gray and Fuller.[4,7] Previously, the effective parasitic current when the electrode was held at open circuit was found to be 22 $\mu A/cm^2$.[4]

The experiments with MSC, melts B, C, and D, show some distinct differences from those with MPIC, melt A. The cyclic voltammograms for melt B and C are shown in Fig. 3. The plating of sodium in melt B was observed at potentials negative of −2.4 V and the oxidation of sodium was seen at potentials positive of −2.4 V on the positive-going scan. The coulombic efficiency was 77% and the current density was low. Melt C, with a larger ratio of MSC to $AlCl_3$, dissolves more NaCl, and exhibits both higher current efficiency (91%) and higher current densities.

A chronoamperogram of an electrode in melt C is shown in Fig. 4. The potential was held at −2.6 V for 100 s, and then stepped to −0.75 V where oxidation and dissolution of the sodium occurred. The coulombic efficiency was found to be 97%, the highest achieved for the plating/stripping of sodium in this type of room-temperature melt. Clearly, the higher sodium loading (longer plating time) at the negative voltage limit (potential stepped to −2.6 V and not scanned) resulted in more of the current being used for sodium

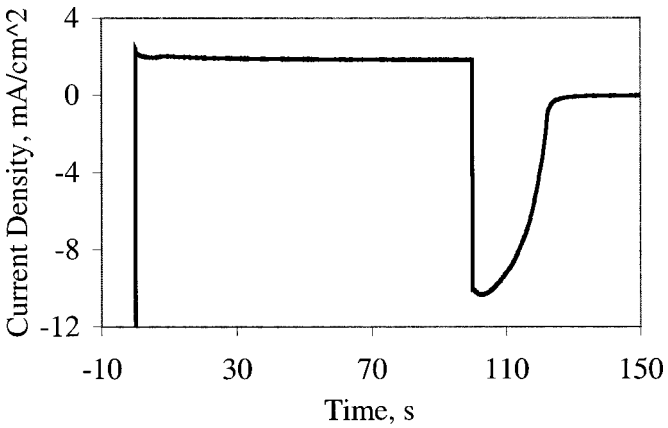

Figure 4. CA on platinum for 35/65 MSC melt. Deposition was at −2.6 V for 100 s. Stripping was at −0.75 V until zero current.

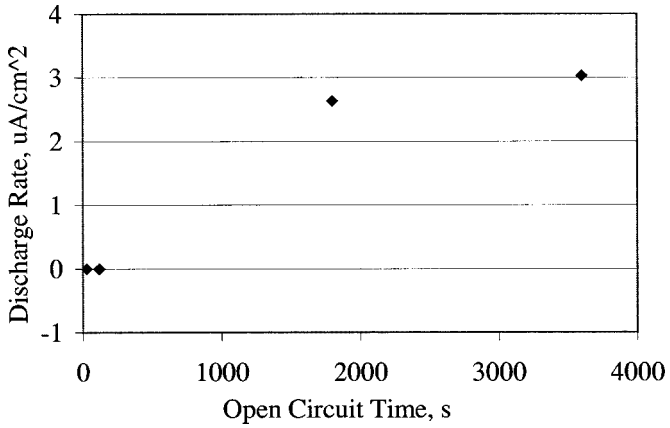

Figure 5. Self-discharge rate of sodium plated on platinum electrode in the 35/65 MSC melt (melt C).

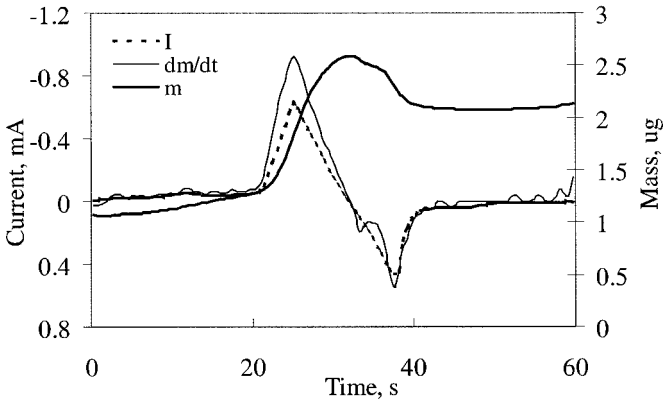

Figure 7. CV (v = 100 mV/s) on platinum for 27/73 MSC melt (melt D). Area of platinum is 0.196 cm^2.

plating. Further, almost all of this sodium is oxidized on stripping, showing little reaction with the electrolyte. Note also the very high current density on stripping, over 10 mA/cm^2.

Experiments investigating the effect of open-circuit potential on the loss of plated sodium corroborate the slow reaction between the sodium and the electrolyte. When held at open circuit for 1 h, 76% of the sodium was recovered (electrochemically oxidized). Figure 5 shows the effective self-discharge rate as a function of open-circuit time, stabilizing near 3 $\mu A/cm^2$. This self-discharge rate is about seven times less than that observed in the MPIC melt.

The effect of sodium ion concentration is quite dramatic. The cyclic voltammogram of melt C is shown in Fig. 6. The dissolved NaCl concentration was 1.0 M, rather than the 2.5 M used in the previous experiments. The plating current is similar to that achieved with the 2.5 M NaCl concentration; however, the coulombic efficiency in Fig. 6 is only 13%. This suggests that at the highest currents (most negative potentials), the sodium ion concentration at the electrode surface is partially depleted, resulting in electrolyte degradation or dissolution of a protective layer formed on the plated sodium. If a protective layer was composed of NaCl, it would be readily dissolved back into solution, and sodium ions would be available for reduction.

It was hoped that melt C could be used in EQCM experiments; however, electrode vibration was not possible apparently due to the high viscosity of the melt. For this reason, melt D was constructed by diluting melt C to 73/27 ($MSC/AlCl_3$) and 1.9 M NaCl, and the melt temperature increased above room temperature, *ca.* 50°C. The coulombic efficiency in Fig. 7 (the diluted melt) is only 69%, as compared to Fig. 1 where the efficiency was higher. Note that the mass on the electrode increases well positive of the potential necessary to plate sodium. This reduction of species in the electrolyte results in the creation of insoluble species and an increase in mass on the electrode. Another possible scenario for this excess mass is the formation of protective layers on the electrode and the plated sodium. As described earlier for thionyl chloride in the MPIC melt, there is a possibility that MSC might similarly react with sodium metal. The protective layers may be due to this reaction and result in excess mass during the reduction scan.

On stripping, essentially all of the mass lost can be attributed to sodium oxidation; total mass decrease during oxidation is almost equivalent to the oxidation charge passed. This leads to the fact that unreacted sodium can be completely recovered, and the insoluble product of electrolyte reduction remains on the electrode as sodium was oxidized. After oxidation, a large residual mass remained on the working electrode compared to 17% residual mass observed in the MPIC melt.

All the experiments so far described were conducted at or near 25°C. The effect of increased temperature was explored with melt C. There was no significant effect on coulombic efficiency up to about 50°C; however, the current density increased as temperature rose. At temperatures over 60°C a slight decrease in coulombic efficiency, to about 75%, was observed, but improvement in current density was shown as it increased from 2 mA/cm^2 at room temperature to 10 mA/cm^2 at 63°C.

Improvement of methanesulfonyl chloride melts was achieved by modifying their composition. 97% coulombic efficiency of sodium redox in 35/65 MSC melts was better than any published results. EQCM was able to verify the high stability of sodium metal in the 35/65 MSC systems, which have a 3 $\mu A/cm^2$ self-discharge rate of sodium metal.

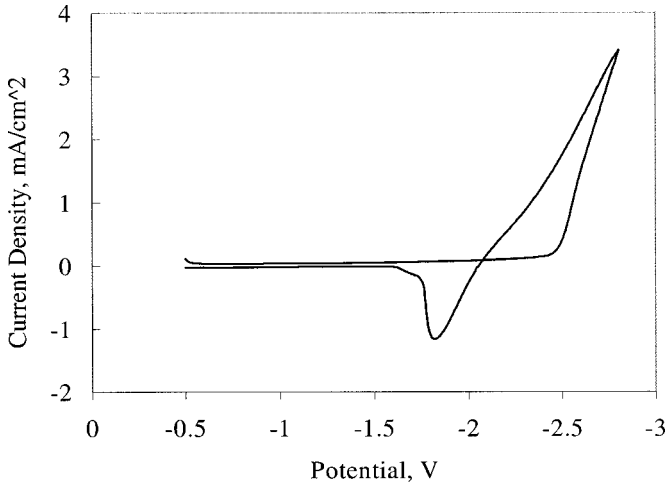

Figure 6. CV on platinum for 35/65 MSC melt with 1.0 M NaCl.

Conclusions

Coincident cyclic voltammetry, chronoamperometry, and EQCM experiments revealed, for the first time, details of the inefficiencies in the plating-stripping of sodium in buffered-neutral MPIC melts. While sodium metal was plating, electrolytes or impurities were also reduced. Sodium metal reacted with either electrolytes or impurities after depletion of sodium ions at the surface of the electrode.

New inorganic liquid-based molten salt electrolytes seem to overcome those limitations of the organic molten salt systems. Melts made from aluminum chloride, MSC, and sodium chloride show high coulombic efficiencies, up to 97%, and very low self-discharge rates, less than 3 $\mu A/cm^2$. The mass stripped during oxidation showed nearly exact correspondence with charge passed (for sodium), verifying the anodic process.

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