Low Temperature Molten Salt Electrolytes Containing Ternary Alkyl Sulfonium Salts

S.D. Jones and G.E. Blomgren

Eveready Battery Company, Inc.
Technology Laboratory
25225 Detroit Road
Westlake, Ohio 44145

Abstract

A new family of low temperature molten salts has been found. These electrolytes are based on the ternary alkyl sulfonium salts in mixtures with inorganic metal halides. A typical composition is the mixture of trimethylsulfonium chloride (TMSC) and AlCl₃ in a 1:2 mole ratio. This melt has a conductivity of 5.5 mS/cm, remains fluid until somewhat below -50°C, and can plate and strip aluminum. TMSC has the same electrochemically stable window as 1-methyl-3-ethylimidazolium chloride.

Introduction

In recent years, considerable attention has been given to low temperature molten salt electrolytes, particularly those that are liquid at room temperature and below. Room temperature melts made from mixtures of inorganic salts such as aluminum chloride with certain organic salts such as N-(n-butyl) pyridinium chloride (BPC), 1-methyl-3-ethylimidazolium chloride (MEIC), or trimethylphenylammonium chloride (TMPAC) have been disclosed (1-3).

Unfortunately, the above melts all have inherent problems associated with them. Melts containing BPC have a foreshortened electrochemically stable window due to reduction of the pyridinium cation. Melts containing MEIC have a significantly larger electrochemically stable window than those containing BPC, however, MEIC is not commercially available and must be specially synthesized. Also, melts containing MEIC are somewhat difficult to prepare due to the rapid and highly exothermic reaction between the MEIC and AlCl₃ that will decompose the MEIC unless special precautions are taken to control the reaction rate. Melts containing TMPAC have the same electrochemically stable window as those made with MEIC and TMPAC is commercially available, however, the conductivity of this melt is considerably lower than the other melts.
Because of the shortcomings of the known melts, an investigation of new compounds capable of forming a low temperature melt with AlCl₃ was undertaken. The family of sulfonium salts was chosen for study. One of these salts, trimethylsulfonium chloride (TMSC), may prove to be a useful battery electrolyte (4).

**Experimental**

The chemicals were dried under vacuum at low heat except for the AlCl₃ (Fluka) which was used as received. The TMSC was synthesized from dimethyl sulfide and methyl chloroformate by the method of Byrne et al. (5). The synthesized TMSC was characterized using a Digilab FTS-80 Infrared Spectrometer with CsI pellets, a Finnigan Model 4021 Automated GC/MS using a glass column packed with 0.2% Carbowax 1500 on 80/100 Carbopack C with the injection port temperature set at 175°C, and a Varian Nuclear Magnetic Spectrometer. A sample of TMSC dissolved in water was obtained from the Stauffer Chemical Company. Trimethylsulfonium iodide (TMSI-Aldrich), which sublimes at 213°C, was dried at 70-80°C under vacuum. The melts were prepared and tested in a Vacuum/Atmospheres stainless steel dri-lab. An MO-40 dri-train kept the moisture content of the dri-lab below 1 ppm and the oxygen content below 20 ppm.

Conductivities of the melts were measured using an ESI 253 Impedance Meter with YSI 3403 Conductivity Cells. Cannon-Fenske viscometers were used for the kinematic viscosity determinations while the densities were determined by the weighing of 5 ml graduated cylinders. All of the above physical properties were measured in the dry box without thermostating. The temperature of the dry box was approximately 27°C.

Cyclic voltammetry measurements were made on a PAR 173 potentiostat equipped with a 276 interface and controlled by an H-P 9816 computer. The working and counter electrodes were glassy carbon. The reference electrode for use with molten salts was an aluminum wire in MEIC:AlCl₃ (0.60 mole fraction AlCl₃) that was separated from the melt by a fine glass frit. The reference electrode for use with acetonitrile solutions was a silver wire in 0.1M tetramethylammonium perchlorate in acetonitrile solution separated from the sample by a fine glass frit.
Results and Discussion

The analytical characterizations of the synthesized TMSC show that it is indeed TMSC. The infrared spectra is shown in Figure 1 with the major peaks assigned. If the methyl groups are assumed to be freely rotating, the cation assumes a $C_3v$ symmetry for the molecular vibrations. In this case, considering the large disparity in mass between the proton and carbon, a separation into skeletal S-C modes (in the $C_3v$ point group) and vibrations characteristic of the methyl group can be reasonably expected. With this assumption, we would expect four allowed S-C vibrations in the infrared. Because of the cationic nature of the ion, the degenerate $v_3$ C-S stretching vibration would be expected to be at a higher frequency than the C-S stretching frequency in dimethyl sulfide, assigned at around 700 cm$^{-1}$ by Trotter and Thompson (5) and by Shepard (6). Therefore, we assigned this vibration to the peak at 930 cm$^{-1}$. We assign the two lower frequency peaks at 710 and 640 cm$^{-1}$ to the symmetric stretching vibration, $v_1$, and the degenerate bending vibration, $v_2$. The symmetric bend, $v_1$, probably occurs at lower frequencies than our observations. The rest of the assignments, due to the methyl group vibrations, are as shown in Figure 1. Several additional small peaks were identified in the as-prepared sample as due to the dimethyl sulfide starting material and were easily removed with a water wash.

The proton NMR exhibits a single peak as would be expected from the symmetrical shape of TMSC, again assuming free rotation of the methyl groups. A literature reference (7) indicated that the single peak would be at 2.88 ppm in D$_2$O but we found that the peak occurred at 3.12 ppm in either D$_2$O or trifluoroacetic acid. The TMSC appears to thermally degrade into methyl chloride and dimethyl sulfide when subjected to either solid probe/mass spectroscopy or gas chromatography/mass spectroscopy. However, these would be the expected decomposition products and the technique shows no difference in the TMSC that was synthesized in-house and that obtained from Stauffer.

The newly discovered melts are made up of a mixture of an inorganic metal halide such as AlCl$_3$ and a ternary alkyl sulfonium salt such as trimethylsulfonium chloride or iodide. We believe that the relatively large sulfur atom with its hybridized 3p electrons can be easily polarized and acts similarly to an aryl group with its pi electrons (8). This increases the interaction between the cation and the easily polarizable chloroaluminate anions and lowers the melting point of the mixture. Other factors which
contribute to melting point lowering are the delocalized nature of the interaction (induced dipole-induced dipole) and the low lattice energy of the crystalline salts (8). The striking fact in this work is that small methyl rather than large aryl substituents can accomplish the melting point lowering if the central atom is large and polarizable.

DSC measurements failed to show a freezing point or melting point for the TMSC:AlCl₃ (1:2) melt. Visual observations of the melt showed that solidification occurred somewhat below -50°C. On warming, the mixture stayed solid until about -5°C where it became a thick, viscous liquid. This indicates that on cooling, the melt becomes a supercooled liquid that probably has a glass transition point rather than a freezing point. The TMSI:AlCl₃ (1:2) mixture required gentle heating to become molten, but then remained a light yellow liquid at ambient temperature. It is assumed that the light yellow color comes from a small amount of iodine or triiodide ion present in the solution.

The TMSC:AlCl₃ melt shows a conductivity of 5.5 mS/cm at the temperature of the dry box, while the TMSI:AlCl₃ melt conductivity was 4.5 mS/cm. These values are intermediate between TMPAC (or BPC)/aluminum chloride melts, and the cyclic MEIC/aluminum chloride melt, and they are much higher than the large aromatic sulfonium ions discussed previously (see (8) for data comparisons and discussion). The measured viscosity for the TMSC melt was 39.3 cP and the density 1.40 g/cm³, both at dry box temperature. The viscosity is higher than MEIC, BPC or TMPAC in combination with aluminum chloride, while the density is comparable with MEIC and slightly larger than TMPAC or BPC. Clearly, there is an interaction of effects since the TMSC has the lowest molecular weight of the four salts and might therefore be expected to have the most mobile cation of the four, giving rise to higher conductivity and lower viscosity. Although only one of the atoms on the aluminate anion is iodide in the TMSI case, one might expect a larger effect compared to TMSC if the anion mobility were controlling. Therefore, we conclude that the cation mobility is more important.

The cyclic voltammogram of the TMSC:AlCl₃ (0.67) melt is shown in Figure 2. It can be seen that aluminum will plate and strip from this acid melt in a manner very similar to acid melts made with MEIC or TMPAC (8). The plating and stripping of aluminum has also been done by cycling two aluminum electrodes at 0.5 mA/cm², but shape change due to electrolyte stratification was a problem as seen before (8). Figure 3 shows the cyclic voltammetry results for 20
mM solutions of TMSC and MEIC in acetonitrile. It can be seen that the inherent electrochemical stability of TMSC is nearly identical to that of MEIC and TMPAC on both anodic and cathodic sides and considerably better than BPC. Figure 4 shows a cyclic voltammogram for the TMSI:AlCl₃ (0.67) melt. The aluminum deposition and stripping look similar to the other solutions, but the anodic sweep shows high currents at much lower potentials. Subsequent sweeps show interference with aluminum deposition unless the region of anodic current (higher than 1400 mV) is avoided, in which case the peaks are normal. Figure 5 shows the voltammetry of TMSI in AN which indicates that the low voltage oxidation is inherent in the TMSI. Figure 6 shows voltammograms for successive sweeps with this solution where cycling limits are +500 and +1500 mV. We attribute the two anodic peaks at 800 and 1100 mV to the reactions:

\[ 3I^- \rightarrow I_3^- + 2e \quad [1] \]
\[ 2I_3^- \rightarrow 3I_2 + 2e \quad [2] \]

respectively. The cathodic peak at about 900 mV is the reverse of [2]. It is smaller in size than the anodic peak because the following reaction occurs in solution:

\[ I_2 + I^- \rightarrow I_3^- \quad [3] \]

[3] accounts for the decrease in the anodic peak at 800 mV and the growth of the anodic peak at 1100 mV with subsequent scans. The reverse of [1] is not observed in the region which was scanned. Similar voltammetry effects have been observed on platinum electrodes in iodide solutions of organic solvents with a supporting electrolyte (9). In the cited work, however, a side reaction with tetrahydrofuran complicated the results. One of the surprising results from our work on TMSI is that, although the iodide ion is undoubtedly complexed to aluminum in the melt, the solution behaves very much like the simple iodide, iodine, triiodide system seen with the uncomplexed salt in organic solvents. The narrower voltage range of the TMSI solutions and the effects on aluminum deposition and stripping limit the usefulness of this salt compared to TMPAC and MEIC, but the work illustrates the usefulness of these media for studying electrochemical reactions.

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Figure 1

CYCLIC VOLTAMMETRY COMPARISON
20 mMolar in a solution of 0.1 Molar TMAP in AN

Figure 3

Figure 2

TMSI·AlCl₃ (0.67)

Figure 4

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CYCLIC VOLTAMMETRY COMPARISON

20 mMolar in solution of 0.1 Molar TMAP in AN

TMSI in TMAP/AN
20 mMolar in a solution of 0.1 Molar TMAP in AN

Figure 5

Figure 6