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Electrorefining reaction of sodium in
sodium-bis(trifluoromethylsulfonyl)imide and tetraethylammonium-bis
(trifluoromethylsulfonyl)imide mixture ionic liquid

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Abstract

To develop a electrorefining process of sodium for the recycling of used sodium-sulfur secondary battery, a non-aqueous electrolytic melt was investigated as a candidate for the process. A mixed ionic liquid of NaTFSI(sodium-bis(trifluoromethylsulfonyl)imide) -TEATFSI(tetraethylammonium-bis(trifluoromethylsulfonyl)imide) was selected for the electrolyte, since it has a wide potential window and a weak reactivity with metallic sodium. From AC impedance measurements, the maximum electric conductivity of 36 mS cm⁻¹ was found for a concentration of 20mol%NaTFSI-TEATFSI at 433 K. The cathodic deposition of liquid sodium, 99.99% pure, was obtained on a glassy carbon electrode by constant current electrolysis. The calcium concentration in the sodium was decreased from 500 to 12 ppm by the electrorefining. A cathodic current efficiency at 88% was achieved in these electrorefining experiments.

Keywords: sodium-sulfur secondary battery, electrorefining of sodium, ionic liquid, recycling of metallic sodium,

1. Introduction

Recently, batteries have been used in load leveling of electric power, emergency power supplies alleviating electricity interruptions in factories, and storage devices for power generated by solar or wind energy. Here, the Na-S battery has a number of advantages such as high energy density, low material costs, long useful lifetime, and little need for complex maintenance ¹⁻⁴⁾ and commercial scale production of such batteries has taken place since 2003. ⁵⁾

The useful lifetime of Na-S batteries is about 15 years and large numbers of used Na-S batteries will begin to be discarded in the near future. In used Na-S batteries, metallic sodium and sodium polysulfide remain in the batteries. Metallic sodium is an active metal, and treatment of sodium in water poses difficulties. Thermal disposal of used Na-S batteries has been proposed, however no effective recycling process for Na-S battery components has been developed. We have proposed a sodium recycling process which involves collection of the metallic sodium from the used Na-S batteries and a refining process for the collected metallic sodium. ^{6,7)}

The sodium electrowinning process (Downs process) can not be used in refining the metallic sodium ^{8,9)} as raw materials for the electrowinning process is chloride or oxide. The Electrorefining is used in refining of crude metals, but an electrorefining process for sodium has not been implemented on an industrial scale. The electrorefining process of metallic sodium from the used Na-S battery developed by us ⁶⁾ investigated organic solvents, molten salts, and ionic liquids as the electrolytic melt. From the results, it was found that a mixed ionic liquid of NaTFSI (sodium-bis(trifluoromethylsulfonyl)imide) -TEATFSI (tetraethylammonium-bis(trifluoromethylsulfonyl)imide) has a wide electrochemical potential window and that it

displays low reactivity with molten metallic sodium below 473 K. This paper reports the melting point of the ionic liquid system, its conductance, voltammogram, and electrorefining reaction with metallic sodium by constant current electrolysis in the NaTFSI-TEATFSI ionic liquid.

2. Experimental

The NaTFSI (sodium-bis(trifluoromethylsulfonyl)imide) was prepared by HTFSI (bis(trifluoromethylsulfonyl) imide, 99% pure, Kanto chemical) and NaOH(99.99% pure, Merk). The TEATFSI (Tetraethylammonium-bis(trifluoromethylsulfonyl)imide, 99% pure, Kishida chemical) was used as received. In the cooling curve measurements to estimate the melting point, 20g of 0-50mol%NaTFSI-TEATFSI powder were melted at 433 K and the melts were cooled slowly about cooling rate of 6 degree min⁻¹. The cooling curves were measured by a thermocouple connected with digital multi meter (Advantest R6452A). The electrical conductivity was calculated from the resistance at the high frequency limit in impedance measurements. The measurement cell was made of Pyrex glass with 20 ml of 10-30mol%NaTFSI-TEATFSI mixture kept at 433 K. Glassy carbon (GC, Tokai carbon, GC-20) plates of 1 cm² were used as the working and counter electrodes. The electrodes were set in the cell with an inter-electrode distance of 15 mm. A Pt (99.99% pure, Tanaka Kikinzoku Kogyo) wire was used as a quasi reference electrode, and the impedance measurements were carried out with an amplitude of 15 mV and at frequencies from 1 Hz to 20 kHz. In the voltammetry, a GC electrode and a metallic sodium (Aldrich, 99.9% pure, calcium content: 500 ppm) electrode were used as working and counter electrodes. The voltammogram was measured over a potential range of 0.5 to -3.0 V vs. Pt with a scan rate of 1.0 x 10⁻¹ Vs⁻¹

in the ionic liquid. The electrochemical measurements were performed in a glove box under a pure argon gas atmosphere. The impedance and electrochemical measurements were controlled by a potentiostat (Iviumstat, Ivium Technologies B.V.).

Electrolysis was carried out under a constant current of 100 Am^{-2} for 2 h in a 20mol%NaTFSI-TEATFSI electrolytic melt at 433K. The electrodeposit formed by the electrolysis was dissolved in distilled water and analyzed by ICP- atomic emission spectroscopy (Thermo i-CAP6000).

3. Results

3-1 Melting point measurements

The melting points of the 0-50mol%NaTFSI-TEATFSI mixtures were determined by the temperature at the plateau (from liquid to solid) in the cooling curves. The relation between the melting point and composition of the 0-50mol%NaTFSI-TEATFSI ionic liquids is shown in Fig. 1. Fig. 1 shows that the melting point decreases with increased addition of NaTFSI to 20mol% and that the melting point increases with NaTFSI addition from 20 to 50mol%. The minimum melting point of the NaTFSI-TEATFSI ionic liquid is 309 K at 20mol% NaTFSI-TEATFSI.

3-2 Conductance measurements

To investigate the electrical conductivity of the NaTFSI-TEATFSI ionic liquids, AC impedance measurements were carried out in 10 - 30mol%NaTFSI concentrations at 433 K. The electrical conductivities were calculated by the values from a high frequency limit, electrode with a cell constant which was measured by 1 mol kg^{-1} potassium chloride solution at 298 K. The electrical conductivity is shown as a function

of the concentration of NaTFSI in Fig. 2. It is seen that the maximum conductivity was 36 mScm^{-1} at 20mol%NaTFSI-TEATFSI.

Taken together the results of the melting point and conductance determinations suggest that a 20mol%NaTFSI melt was suitable and in the following electrochemical treatment, a 20%NaTFSI-TEATFSI melt was selected for the further investigation.

3.3 Voltammogram

A voltammogram on the GC electrodes in the 20mol%NaTFSI-TEATFSI at 433 K is shown in Fig. 3, here the potential was scanned from 1.0 to -3.0 V at a sweep rate of $1.0 \times 10^{-1} \text{ Vs}^{-1}$. When the potential is as scanned from 1.0 V to the negative direction, a cathodic current started to flow at -1.5 V, and increased until -3.0 V, where the current density reached 400 Am^{-2} . A grey electrodeposit was observed on the surface in the cathodic current potential region. When the potential was reversed at -3.0 V, an anodic current flowed from -2.4 to 0.0 V, and the grey electrodeposit formed in the cathodic scan had completely disappeared at 0.0 V.

3.4 Electrorefining of metallic sodium

The electrorefining experiment was performed under a constant current of 100 Am^{-2} for 2 h between an anode of metallic sodium containing 500 ppm of calcium and a GC cathode in 20mol%NaTFSI-TEATFSI at 433 K. The potential of the cathode measured against the Pt electrode is shown in Fig. 4. The potential shows almost constant values at about -2.5 V vs. Pt. After the electrolysis, liquid electrodeposit floated around the GC cathode, and Fig. 5 is a photograph of this liquid electrodeposit. From the photograph, it was found that liquid spheres of about 3 mm diameter were formed

around the GC cathode. After the electrolysis, the electrolyte was removed and the leaching electrolyte on the electrodeposit was wiped off the GC cathode with paper tissue. The electrodeposits were dissolved into distilled water where the pH was controlled by 0.01M HNO₃ solution, and the solution was analyzed by ICP-AES.

The ICP-AES showed that the electrodeposit formed by the constant current electrolysis consisted of metallic sodium of 99.99 % purity with 12 ppm of metallic calcium as an impurity. The calcium content of the impurity had decreased to about one fortieth of the original 500 ppm by the electrorefining process.

4. Discussion

The electrical conductivity of the NaTFSI-TEATFSI ionic liquid exhibited a maximum at 20mol%NaTFSI and was lower both at higher and lower concentrations of NaTFSI. This is strongly correlated with the viscosity of the NaTFSI-TEATFSI ionic liquid. Since the concentration of sodium ions in the ionic liquid increases with increases in NaTFSI, the electrical conductivity may also be expected to increase. However, addition of more than 20mol%NaTFSI raises the viscosity in the ionic liquid system, and would be a cause of the decrease in electrical conductivity. The phenomenon would be similar to that of lithium salt dissolved in organic solvents.¹⁰⁾ From the electrical conductance results, the 20mol%NaTFSI-TEATFSI ionic liquid was selected as the optimum electrolyte for the electrorefining of sodium.

In the voltammogram in Fig. 3, a pair of reduction and oxidation currents was observed in the electrolyte. Since the only metallic cations in the electrolyte is sodium ions, the currents would correspond to the electrodeposition and electrodisolution of sodium. A comparison of the electric charge of the cathodic reduction and the anodic

dissolution shows that the cathodic charge is slightly larger than the anodic one. The reason for the difference may be due to the consumption of metallic sodium reacting with a small amount of water contained in the electrolyte to form sodium oxide.

In the electrorefining experiment in Fig. 4, the potential of the GC cathode was almost constant at about -2.5 V showing that only the electrodeposition reaction takes place during the electrolysis.

The total amount of electrodeposited sodium was evaluated by the ICP analysis of a solution with all the cathodic electrodeposits dissolved. The cathodic current efficiency was calculated from the ratio of the amount of the deposit to the amount that should have been deposited based on the electric charge passed during the electrorefining. The current efficiency estimated in this manner was 88% and the remaining 12% can be ascribed to the fine sodium particles dispersed in the solution and that it was not possible to collect. The concentration of calcium in the electrodeposited sodium greatly decreased from that in the original metallic sodium anode. Because the equilibrium potential of Ca/Ca^{2+} in the electrolyte is less noble than that of Na^+/Na , the calcium of the anode is preferentially dissolved, but cathodic deposition of calcium is strongly suppressed.

This result shows that in the sodium electrorefining by 20mol%NaTFSI-TEATFSI ionic liquid at 433 K investigated here, it is possible to electrodeposit liquid sodium and efficiently remove calcium containing crude sodium. This process may be practical as a technique for the production of very pure metallic sodium.

5. Conclusions

To develop an electrorefining of sodium process, the physical and electrochemical

properties of ionic liquids of NaTFSI-TEATFSI were investigated.

The results may be summarized as follows:

- (1) The maximum electrical conductivity at 433 K is 36 mScm^{-1} in 20mol%NaTFSI-TEATFSI.
- (2) Cathodic reduction of sodium ions starts at potentials of -1.5 V vs. Pt and anodic dissolution of the sodium starts from -2.4 V in the electrolyte.
- (3) Metallic sodium, 99.99% pure, was obtained with an anode of sodium containing 500 ppm of calcium by the electrorefining process.

Acknowledgement

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Figure and captions

Fig. 1 Relationship between melting point and composition of NaTFSI-TEATFSI ionic liquid.

Fig. 2 Relationship between electrical conductivity and concentration of NaTFSI in TEATFSI ionic liquid at 433 K.

Fig. 3 Voltammogram on GC electrodes in the 20mol%NaTFSI -TEATFSI ionic liquid at 433 K.

Fig. 4 The potential change during electrorefining between the metallic sodium anode and metallic sodium cathode under the constant current of 100 Am^{-2} in 20mol%NaTFSI- TEATFSI ionic liquid at 433 K.

Fig. 5 Photograph of liquid sodium metal on the GC cathode in the electrolyte after electrolysis at 433 K.

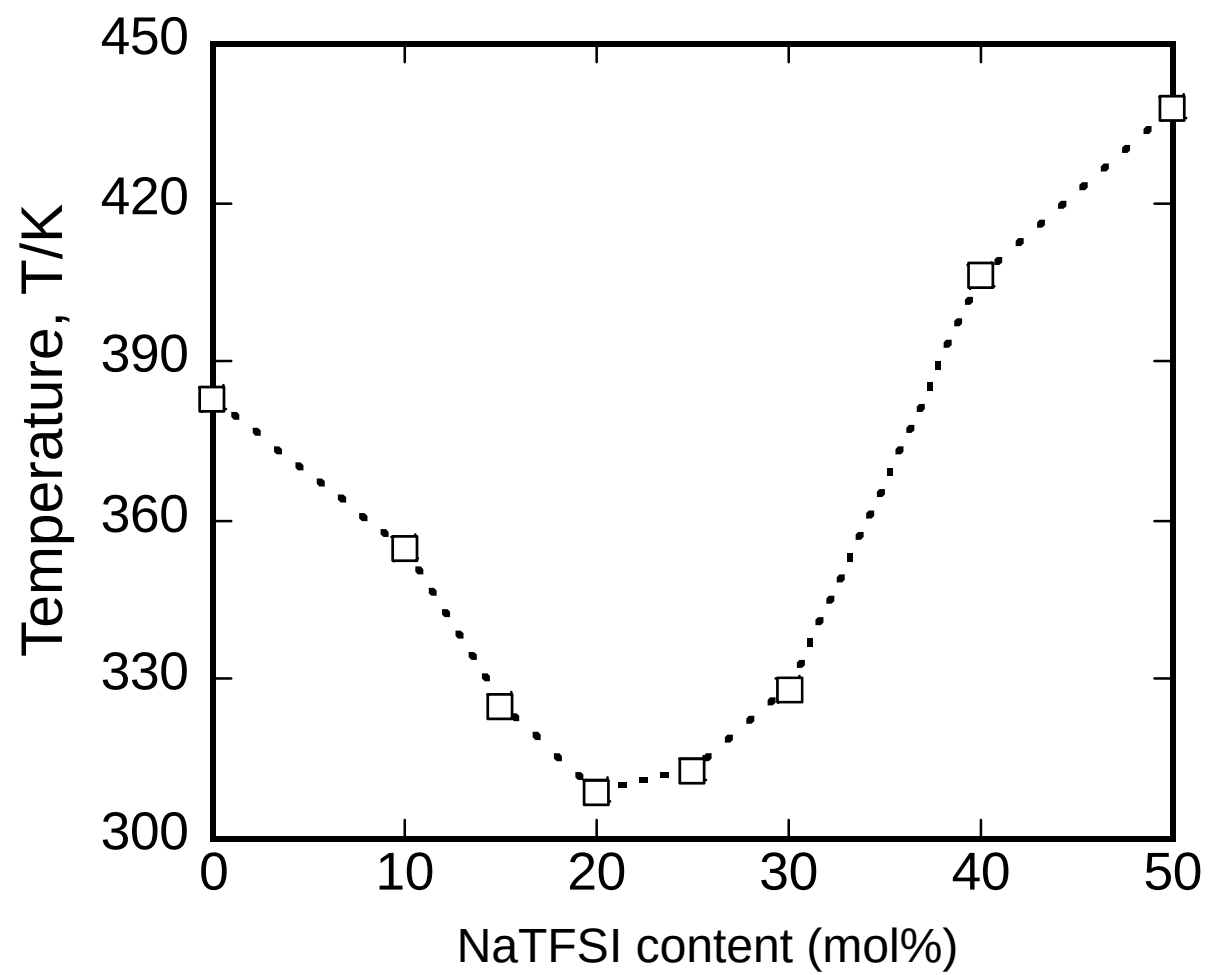


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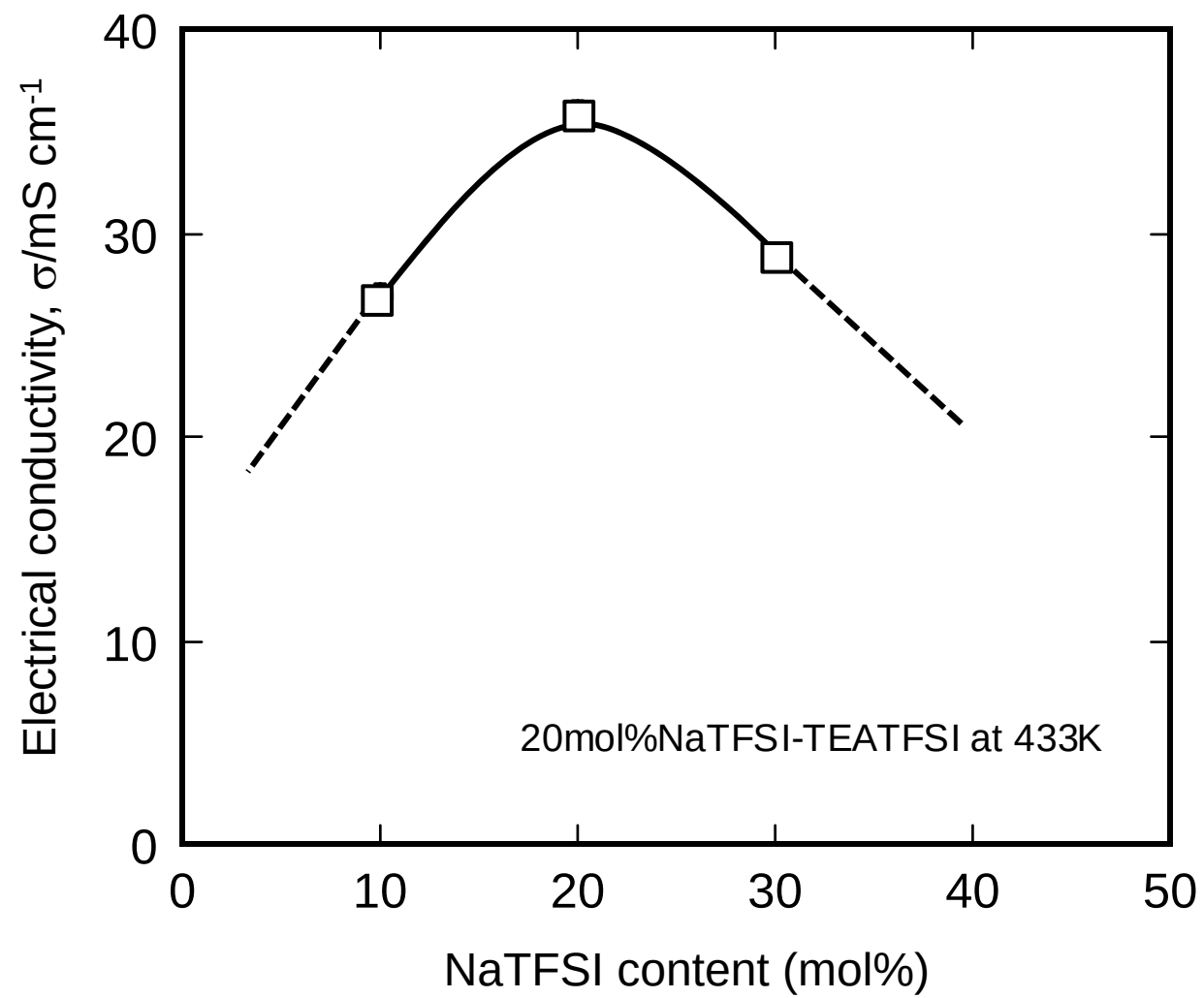


Fig. 2 Relationship between electrical conductivity and concentration of NaTFSI in TEATFSI ionic liquid at 433 K.

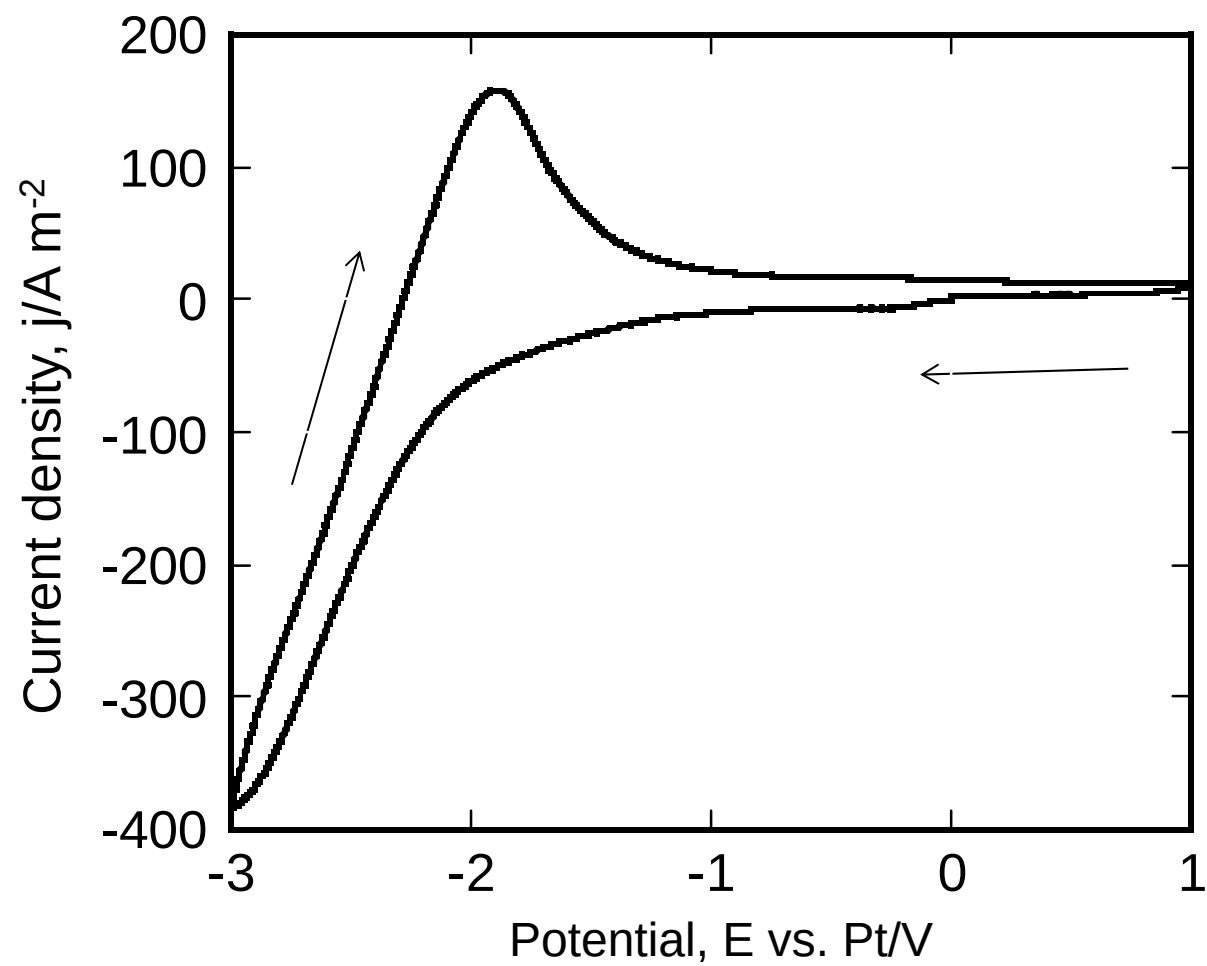


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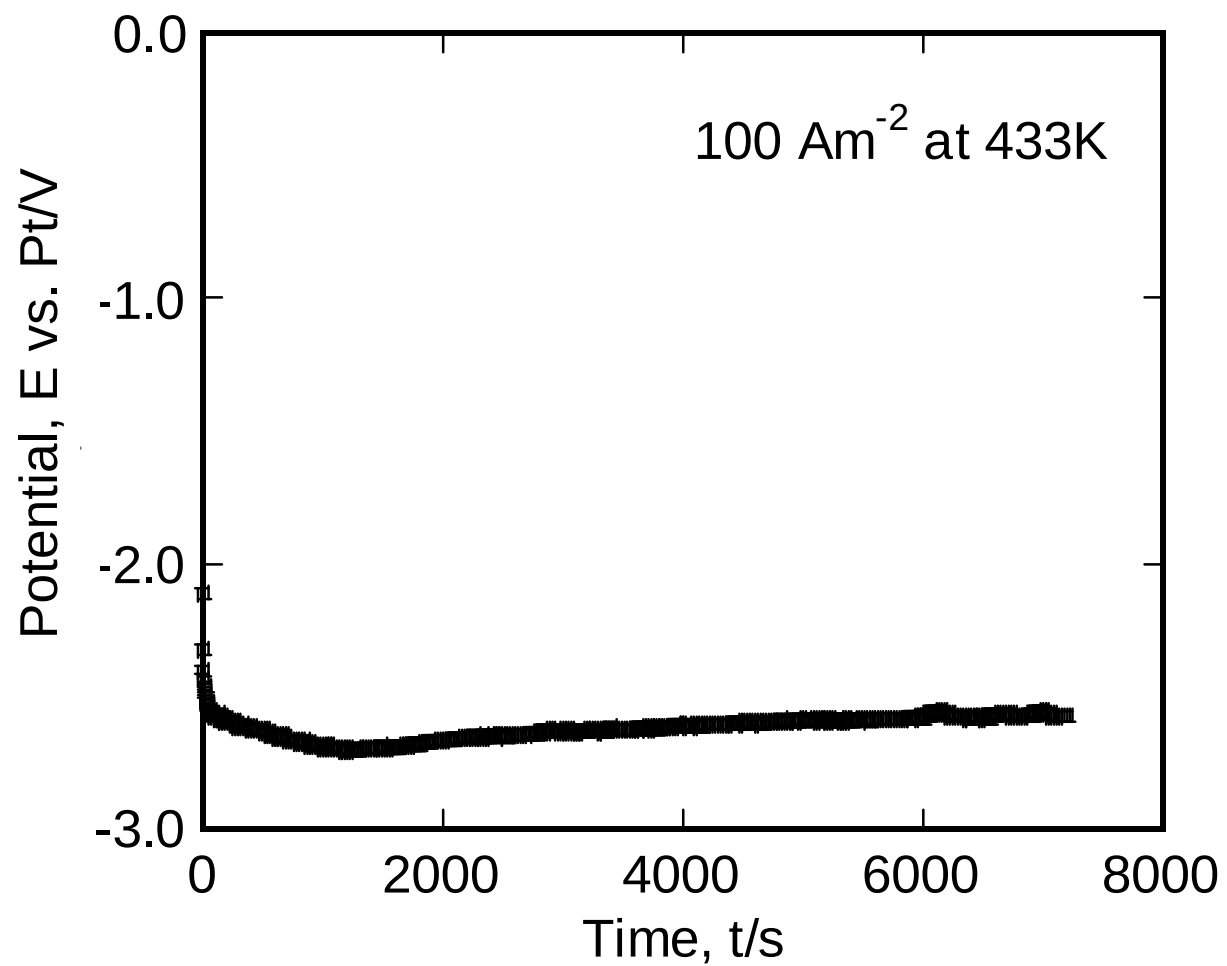


Fig. 4 The potential change during electrorefining between the metallic sodium anode and metallic sodium cathode under the constant current of 100 Am^{-2} in 20mol%NaTFSI- TEATFSI ionic liquid at 433 K.

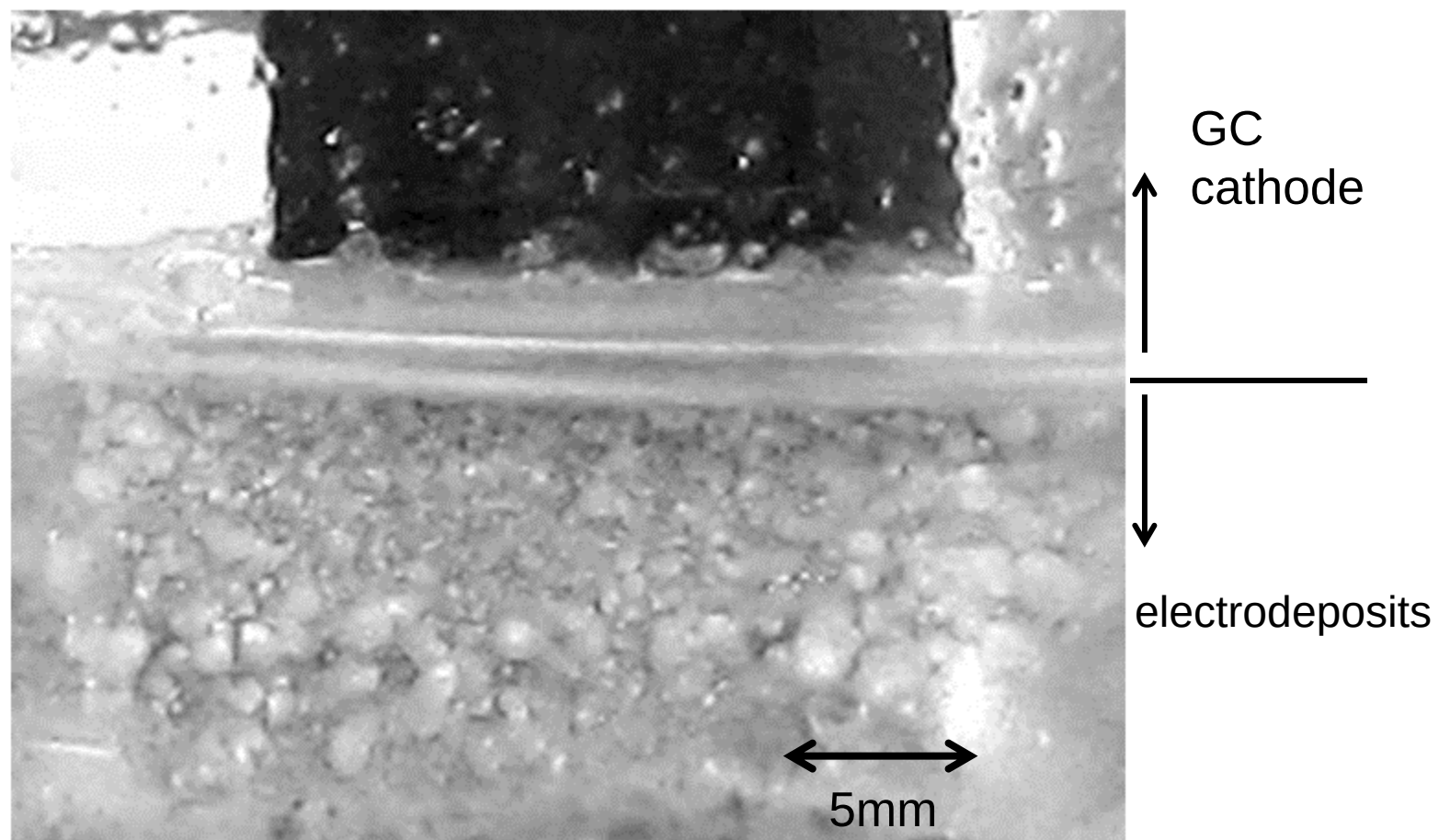


Fig. 5 Photograph of liquid sodium metal on the GC cathode in the electrolyte after electrolysis at 433 K.