JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

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Electrical Conductivity of Molten Fluoride–Chloride Electrolytes Containing K_2SiF_6 and SiO_2

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S Supporting Information

ABSTRACT: The electrical conductivity of fluoride–chloride electrolytes for solar silicon electrolysis was investigated using impedance spectroscopy. Electrolytes containing potassium fluoride, potassium chloride, cesium chloride, potassium hexafluorosilicate, and silicon oxide were studied. The influence of the electrolyte composition on the electrical conductivity was examined.

INTRODUCTION

The production of solar-grade silicon is very important for the development of "green" energetics. Solar-grade silicon dioxide is a potential raw material. It is possible to perform electrolysis of SiO_2 in a molten salt bath.[1] Electrolytic deposits of silicon nanoneedles have been obtained via this method. These silicon structures can be used for the development of lithium batteries that exhibit a high specific electric capacity.

The choice of electrolyte is very important for the electrolytic process. Fluoride–chloride melts have several advantages. First, these electrolytes possess low vapor pressure because of the strong chemical interaction of silicon ions with large alkali cations (potassium, cesium), which decreases the electrolyte loss. Second, it is possible to perform the electrolysis at relatively low temperatures (923–1023 K). At these temperatures, good construction materials are available, and it is possible to obtain nano- or microneedle deposits.[2] The most important advantage of fluoride–chloride melts is the relatively high silicon oxide solubility at high concentrations of fluoride salts. These melts also possess high electrical conductivity. The data on the electrical conductivity of molten electrolytes that are prospects for electrolytic production of solar silicon are very limited. There is only one publication with data presented in graphical form.[3]

EXPERIMENTAL SECTION

The investigation of the electrical conductivity of halide–oxide melts is challenging because of their high corrosion activity. Special requirements for the construction materials for the measurement cell must be followed to obtain reliable experimental data. The capillary cell provides better accuracy in comparison to the Eger-type cell.[4] The most difficult problem with the capillary cell is the choice of capillary material. The most aggressive part of the electrolyte is the fluoride salt. Over the last 20 years, pyrolytic boron nitride has primarily been used for fluoride melt measurements.[5,6] A detailed description of the conductivity measurements can be found in our previous publications.[7,8]

Materials. The electrolytes were prepared from "chemically pure" grade CsCl, KCl, and KF·HF as well as "pure for analysis" grade K_2SiF_6. Potassium chloride was obtained from Uralkalii, and KH·HF, CsCl, and K_2SiF_6 were obtained from Vekton. A mixture of KCl and KF·HF was heated in a glassy carbon crucible to 973 K and kept at this temperature for (4 to 5) h. All of the HF was removed via the thermal decomposition of KF·HF, and then the K_2SiF_6 was added. The melt was stirred constantly for 30 min and then transferred to a graphite crucible. The as-prepared electrolytes were stored in a drybox.

Experimental Cell. Two types of conductivity cells were used to determine the electrical conductivity of the electrolytes in this study (Figure 1). The first was a capillary cell, and the second was a cell with two parallel electrodes. Boron nitride was selected as the capillary material because it exhibits high corrosion resistance in fluoride melts, a small heat-expansion coefficient, and a high electrical resistance (i.e., it behaves as an insulator) even at 1273 K. The capillary unit consisted of a boron nitride rod (San Gobain Ceramics) in which a 1.5–2 mm diameter capillary was drilled. The platinum electrode placed in the upper part of the capillary unit was twisted into a spiral to increase the surface area of the electrode submerged in the molten electrolyte. The capillary unit was hung on the second platinum electrode. This type of capillary cell is similar to the cell design proposed by Smirnov.[4] A glassy carbon crucible filled with a weighed amount of the electrolyte was placed on the bottom of a quartz tube that was tightly closed by a vacuum rubber plug, which contained holes for the electrodes, thermocouple, and the inert gas inlet and outlet. The small tubes for the gas inlet and outlet and the cases for the thermocouple and electrodes were prepared from alundum. The platinum/platinum–rhodium thermocouple was immersed directly into the melt without a case.

The difference between the cell with the parallel electrodes and the capillary-type cell was that the two rigidly fixed parallel molybdenum electrodes were immersed into the melt. The unit used to load the additives into the molten electrolyte in a flow of an inert gas was attached to the small alundum gas-feeder tube. The cell with the parallel electrodes was used for measurements of melts containing SiO_2.

Special Issue: Kenneth N. Marsh Festschrift

Received: July 13, 2011
Accepted: October 12, 2011
Published: October 27, 2011

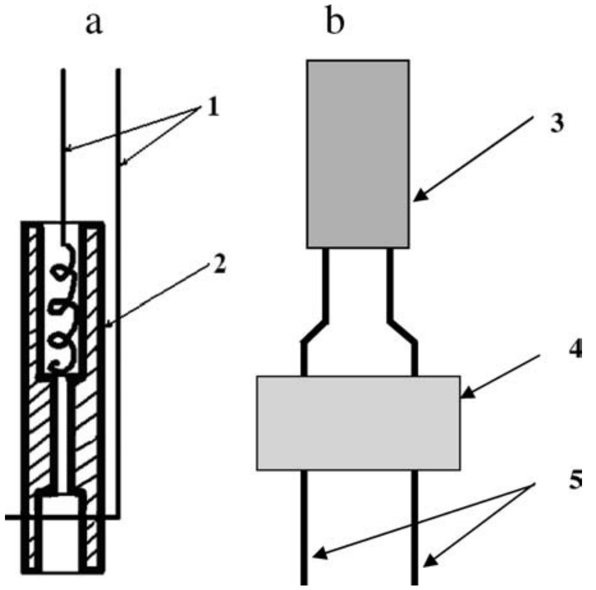

Figure 1. Measurement cells. (a) Capillary: 1, platinum electrode; 2, boron nitride capillary. (b) Parallel electrodes: 3, alundum case; 4, boron nitride restrictor; 5, molybdenum electrodes.

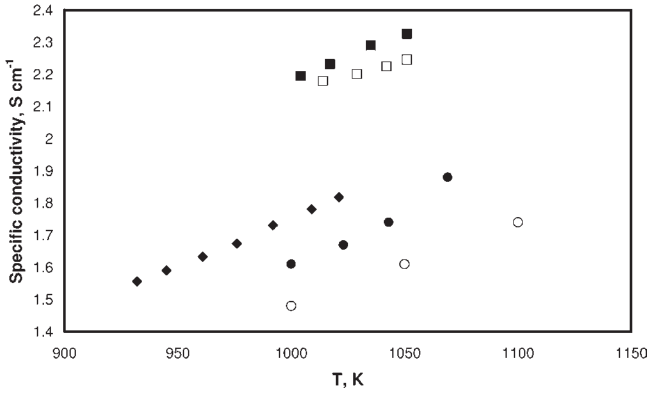

Figure 2. Temperature dependence of the specific conductivity for the following electrolytes (mole fractions given in parentheses): □, KF(0.60)−KCl(0.30)−K_2SiF_6(0.10); ■, KF(0.65)−KCl(0.25)−K_2SiF_6(0.10); ●, KF(0.14)−KCl(0.64)−K_2SiF_6(0.22); ○, KF(0.14)−KCl(0.64)−K_2SiF_6(0.22) (ref 3); ◆, CsCl(0.43)−KCl(0.23)−KF(0.29)−K_2SiF_6(0.05).

Measurement Procedure. The impedance measurements were made using a ZAHNER-Elektrik IM6E impedance measurement unit. The impedance diagrams were recorded over the frequency range from 100 Hz to 100 kHz using a signal with an amplitude of 5 mV. The electrolyte resistance determined from the impedance diagrams was used in the calculation of the electrical conductivity. The capillary cell was calibrated with molten KCl. This salt was dried under vacuum at 673 K and then purified by zone melting. The measurements were performed at (1063 to 1133) K. The specific conductivity data for molten KCl were taken from Janz.[9] The cell constant slightly decreased with temperature. The change was approximately 2 % per 100 K. This dependence was approximated by the linear equation

$$K = A - BT$$

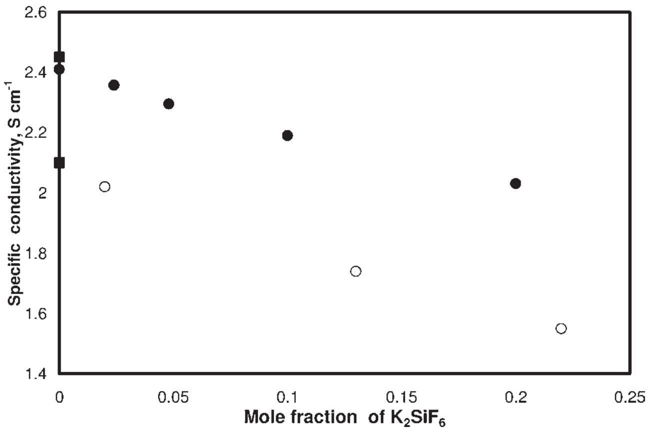

Figure 3. Specific conductivity isotherm as a function of K_2SiF_6 mole fraction at 1023 K: ●, KF/KCl mole ratio = 2 (our data); ○, KF/KCl mole ratio = 0.22 (ref 3); ■, Smirnov's data for the KF−KCl system (ref 10).

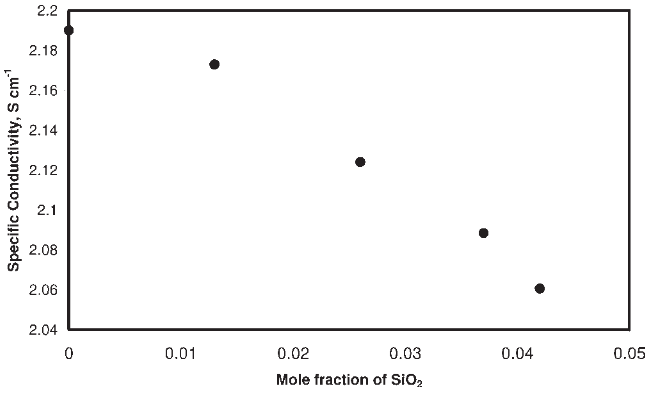

Figure 4. Specific conductivity isotherm upon addition of SiO_2 in the melt initially containing KF(0.60)−KCl(0.30)−K_2SiF_6(0.10) at 1011 K (numbers in parentheses are mole fractions).

in which K is the cell constant, A is a constant, B is the temperature coefficient, and T is the absolute temperature. The constant for the different capillaries varied from (35 to 50) cm^{-1}. The accuracy of the electrical conductivity measurement using the capillary cell was ± 2 %.

The constant of the cell with the parallel electrodes was determined from the electrical conductivity values obtained in the capillary cell. The electrical conductivity was calculated by taking into consideration the temperature dependence of the cell constant. The cell constant for the parallel-electrode cell was (1.2 to 1.5) cm^{-1}. The accuracy of the measurements using the cell with the parallel electrodes was ± 3 %.

■ RESULTS AND DISCUSSION

The temperature dependence for key melt compositions is shown in Figure 2. The dependence of the electrical conductivity on the K_2SiF_6 and SiO_2 concentrations are presented in Figures 3 and 4. The addition of 20 mol % K_2SiF_6 decreased the electrical conductivity from (2.41 to 2.03) S cm^{-1} at 1011 K. The addition of 4 mol % SiO_2 decreased the electrical conductivity from (2.19 to 2.06) S cm^{-1} at 1011 K. The data obtained for the KF−KCl melts are in good agreement with the values reported in the literature.[9] The electrical conductivity of the melt containing 0.67 mole fraction of KF and 0.33 mole fraction of KCl was found to be 2.41 S cm^{-1} at 1023 K. Smirnov and co-workers reported an electrical conductivity of 2.45 S cm^{-1} for the composition containing 0.63 mole fraction KF and 0.37 mole fraction KCl at the same temperature. For KF−KCl−K_2SiF_6 mixtures, there is only one publication by Delimarsky et al.[3] that provides results for compositions rich in chlorides. A comparison of the experimental data for the same composition reveals a key difference between our results and those of Delimarsky et al. The literature values are lower in the region rich in fluoride salts, which can be explained by the difference in the experimental procedures. The measurements in the cited work were performed in an experimental cell with a quartz capillary. Quartz has very low corrosion stability in fluoride melts, and it is very difficult to obtain stable experimental results for fluoride salts in a quartz capillary. The electrical conductivity of KF obtained in this work is significantly lower (2.95 S cm^{-1} at 1136 K) than the literature value for this salt (3.30 S cm^{-1} at 1136 K).[3] The most conductive salt in the mixtures studied is KF, but its concentration is limited by its liquidus temperature and its mole relation to K_2SiF_6, which greatly affects the solubility of silicon oxide. The concentration of K_2SiF_6 is limited by the liquidus temperature and vapor pressure. The chloride concentration is limited by the solubility of SiO_2. Our results cover all possible compositions of suitable electrolytes for pure silicon production from molten salts. Other properties, such as the SiO_2 solubility, phase diagrams, and density, must be taken into consideration when the electrolyte is chosen.

The electrolytes under investigation include mixtures of compounds with a common cation (K^+) and different anions (F^-, Cl^-, and SiF_6^{2-}). A thermodynamic investigation showed that the enthalpy of mixing in the system with a common cation is much lower than that in systems with a common anion,[11] which means that a change in the cation has more influence on the properties. In systems with a common cation, the properties must change with composition in an ideal fashion. The molar volume in KF−KCl mixtures is approximately additive, and the electrical change occurs without extreme points.[10] The SiF_6^{2-} anion has little influence on the interactions between K^+ cations and Cl^- and F^- anions because of its large size.

■ CONCLUSIONS

1. The electrical conductivity of the KF−KCl−CsCl−K_2SiF_6 melts depends on the KF/KCl ratio, and the additions of K_2SiF_6 and CsCl have been measured at (930 to 1050) K.
2. The addition of 20 mol % K_2SiF_6 decreases the electrical conductivity from (2.41 to 2.03) S cm^{-1}. The decrease in the conductivity can be associated with the addition of a large anion (SiF_6^{2-}), which depresses the alkali cation mobility.
3. The electrical conductivity of KCl−KF−K_2SiF_6 melts as a function of SiO_2 concentration was measured at 1011 K. The addition of 4 mol % SiO_2 decreased the electrical conductivity from (2.19 to 2.06) S cm^{-1}.
4. The data obtained allow for the evaluation of the electrical conductivity of the KF−KCl−K_2SiF_6−SiO_2 system for the measured concentration limits.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Specific conductivities of electrolyte mixtures as a function of temperature and composition. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

This work was supported by the Scientific Program N 19 “Chemical Aspects of Energetics” of the Presidium of the Russian Academy of Sciences.

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