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Electrical Conductivity of Molten Carbonate and Carbonate–Chloride Systems Coexisting with Aluminium Oxide Powder

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Abstract: The electrical properties of composite electrolytes (suspensions) composed of α-Al₂O₃ powder and molten carbonate eutectic (Li₂CO₃–Na₂CO₃–K₂CO₃)ₑut or molten carbonate–chloride mixture 0.72(Li₂CO₃–Na₂CO₃–K₂CO₃)ₑut–0.28NaCl have been investigated by AC impedance method. This system shows a dependence of the electrical conductivity upon the temperature and the α-Al₂O₃ content. The specific electrical conductivity of the α-Al₂O₃/(Li₂CO₃–Na₂CO₃–K₂CO₃)ₑut system can be adequately described by the Maxwell equation for two-phase heterogeneous materials. The regression equation for the dependence of the specific conductivity of the α-Al₂O₃/(Li₂CO₃–Na₂CO₃–K₂CO₃)ₑut composite on the aluminium oxide concentration and temperature was obtained.

Keywords: AC Impedance; Electrical Conductivity; Oxide Powder; Suspension.

1 Introduction

Heterogeneous oxide–salt systems consisting of an oxide solid phase and a molten salt are applied in various fields such as the aluminium production technology, the inorganic materials synthesis, batteries, fuel cells, crystal growth, etc. [1–3]. Alkali carbonate melts and composites on their base have wide application as the electrolytes of molten carbonate fuel cells. In particular, “matrix” molten alkali carbonates (thickened with chemically inert oxide material, such as magnesium and aluminium oxides, lithium aluminate) can be used to improve the performance of carbonate fuel cells [4]. However, the problem of the interaction of the carbonate melt with these “inert” materials remains unresolved.

The electrical conductivity of the working electrolyte is one of the most important characteristics of the fuel cell operation [5–9]. Investigation of the conductive properties of the carbonate melts thickened with the oxide powder allows realisation of the effect of non-conducting filler on the processes of electric charge transfer in high-temperature electrolytes. Mizuhata et al. [4, 5, 9] investigated the electrical conductivity of composites containing up to 40 vol% of molten carbonate electrolyte in a ceramic oxide matrix. The coexistence of these electrolytes with inorganic powders results in interactions between the two phases. These interactions cause some anomalous behavior of the physical and chemical properties of the ionic species involved in the system.

In our previous work [10], the data on reactivities of α- and γ-Al₂O₃ finely dispersed powders in molten carbonate eutectic (Li₂CO₃–Na₂CO₃–K₂CO₃ₑut) and carbonate–chloride mixture 0.72(Li₂CO₃–Na₂CO₃–K₂CO₃ₑut)–0.28NaCl were obtained. Various methods like differential thermal analysis, X-ray diffraction and Raman spectroscopy were used to clarify that the α-Al₂O₃ powder did not chemically interact with the molten carbonate eutectic and the carbonate–chloride mixture in the temperature range of 673 K–793 K.

The goal of our study was to examine the conductive properties of molten carbonate and carbonate–chloride electrolytes coexisting with finely dispersed α-Al₂O₃ powder. The effective conductivity of molten systems thickened with non-conductive solid phase should depend on concentration of solid particles and can be considered using the model of two-phase heterogeneous material.

2 Experimental Section

2.1 Sample Preparation and Certification

Chemically pure grade Li₂CO₃, Na₂CO₃ and K₂CO₃ (“Vekton”, St. Petersburg, Russian Federation) were preliminarily dehydrated under vacuum under stepwise increase in temperature and melted...
in argon atmosphere. The carbonate eutectic mixture Li$_2$CO$_3$ (43.5)–Na$_2$CO$_3$ (31.5)–K$_2$CO$_3$ (25) was prepared by fusion of the weighted portions of the prepared salts. The thoroughly mixed salt mixtures were dried under vacuum at 473 K for 1 h to remove traces of adsorbed water. After drying, the mixtures were heated up to 1073 K in an atmosphere of carbon dioxide. In order to reduce the liquidus temperature of the complex chloride–carbonate composition, the amount of sodium chloride (“Vecton”, St. Petersburg, Russian Federation) added to the carbonate mixture was decided based on the eutectic composition of the Na$_2$CO$_3$–NaCl binary system [11].

The phase compositions of the obtained mixtures and the absence of possible admixtures of adsorbed water and hydroxides were confirmed by X-ray diffraction (XRD) and infrared (IR) absorption spectroscopy. The melting point of the carbonate eutectic (670 K), as determined by the differential scanning calorimetric method, agrees with the literature data [12].

The α-Al$_2$O$_3$ powder with an average particle size equal to 500 nm was synthesised by electrochemical treatment of metallic aluminium in a carbonate melt [13]. The single-phase state of the product was confirmed by XRD and IR spectroscopy. A granulometric analysis showed the uniformity of α-Al$_2$O$_3$ grain size (Fig. 1).

The oxide–salt mixtures were prepared by grinding the specified amounts of salt compositions and aluminium oxide powder in an agate mortar. All operations prepared using chemical reagents and mixtures were carried out in a box in nitrogen atmosphere.

### 2.2 Experimental Techniques

The AC impedance was measured using an impedancemeter Z1500J in a frequency range 20 Hz–1.5 MHz. The cell layout is shown in Figure 2. Two parallel platinum electrodes (diameter of 1.5 mm) were immersed into the electrolyte. Electrodes were fixed in the boron nitride bar, which made it possible to control the depth of the electrode immersion during the experiment. The impedance of the electrochemical cell ($Z$) includes the impedance of the electrodes $Z_e$ (the reactive component) and the electrolyte resistance $Z_r$ (the active component). The resistance of the electrolyte is determined from the impedance diagrams. The value of the real part of the impedance was measured at the point of intersection of the curve with the abscissa axis ($Z_r = 0$).

Specific electrical conductivity was calculated by (1):

$$\sigma = K / R,$$

where $K$ is the cell constant (cm$^{-1}$), and $R$ is the resistance of the electrolyte (Ohm). The cell constant was determined from the conductivity values of the KNO$_3$ melt. The electrical conductivity of this electrolyte is well studied in the temperature range 615 K–780 K [14]. The cell was calibrated under same conditions as in the experiments carried out for determining the electrical resistance of the melts under study, i.e. with a fixed depth of the electrode immersion into the melt and an identical interelectrode distance.

The experiments were carried out in a sealed quartz cell under pure Ar atmosphere. The cell was placed in a furnace, and the temperature was controlled by the temperature-control device VARTA TP-403. Gas space of the experimental cell was evacuated to a residual pressure of $2 \times 10^{-5}$ Torr during a stepwise temperature increase up to the electrolyte melting point. Then the cell was filled with high purity argon and the electrolyte was melted. The temperature was measured by means of a Pt–PtRh thermocouple. At least three parallel measurements were made for each series of experiments. The electrical conductivity detection relative error did not exceed 2.5%.

The salt compositions, α-Al$_2$O$_3$ phase modification and compositions of frozen melts after high-temperature experiments were determined using an automatic X-ray diffractometer Rigaku D/MAX-2200VL/PC (Japan).

Certification of the samples for the presence of possible impurities was carried out by Fourier transform infrared spectroscopy (FTIR) using a TENSOR 27 FTIR spectrometer (Bruker, Germany).

The granulometric composition of α-Al$_2$O$_3$ was investigated using a Malvern Mastersizer 2000 laser diffraction analyser (Malvern Instruments, UK). After the experiments, the samples were taken from the lower and upper parts of the frozen melts to examine the sedimentation stability of the suspensions. They were investigated using the IR spectroscopy method (Fig. 3). It was shown that the ratio of the intensities of the characteristic vibration bands of α-Al$_2$O$_3$ (in the region of 650–500 cm$^{-1}$) and the carbonate anion (in the region of 1400 cm$^{-1}$) remained constant. This fact demonstrates the uniform distribution of the α-Al$_2$O$_3$ phase along the height of the crucible as well as the absence of any sedimentation of finely dispersed aluminium oxide in the melt.

The thickened electrolyte at temperatures above the melting temperature of the eutectic (670 K) can be considered as a dispersion in which the disperse phase (α-Al$_2$O$_3$ powder) is distributed in the liquid (carbonate or carbonate–chloride melt). As aluminium oxide is a dielectric, the effective conductivity of the melt with the uniformly distributed non-conductive particles of aluminium oxide can be
described as a special case of the Maxwell model [15] and expressed by the equation:

$$\sigma = \sigma_L \left( 1 + \frac{3}{\phi} \right) \frac{\phi}{V_c + V_L},$$

(3)

where \(V_c\) and \(V_L\) are the volumes of the spheres and the medium, respectively. In case of thickened carbonate or carbonate–chloride 

melts, \(V_c\) is the volume of the \(\alpha\)-Al\(_2\)O\(_3\) powder, and \(V_L\) is the volume of the molten phase.

3 Results and Discussion

Figure 4 demonstrates the temperature dependence of electrical conductivity of the ternary carbonate eutectic melt. Our results (curve 2) agree well with the literature data [12] (curve 1) in the temperature range 673 K–800 K. Thus, according to [12] the conductivity of the ternary carbonate eutectic melt is equal to 0.33 Ohm\(^{-1}\) cm\(^{-1}\) at 673 K and 0.68 Ohm\(^{-1}\) cm\(^{-1}\) at 773 K. Our data for corresponding temperatures are 0.32 \(\pm\) 0.01 Ohm\(^{-1}\) cm\(^{-1}\) and 0.68 \(\pm\) 0.01 Ohm\(^{-1}\) cm\(^{-1}\).

The next step of our work was to determine the electrical conductivity of electrolytes (suspensions) with varying contents of aluminium oxide (20 and 40 wt%). The obtained results of the temperature dependence of electrical conductivity are given in Figure 4 (curve 3 and curve 4). The coefficients of the approximation equations of the electrical conductivity temperature dependence are given in Table 1.

The electrical conductivities of the suspensions calculated with (2) are shown in Figure 4 by the dotted lines. The volume fraction of dispersed aluminium oxide in the suspension was determined by (3). The density of \(\alpha\)-Al\(_2\)O\(_3\) and the density of the melt were calculated according to the equations given in [12] and [16] respectively. Deviation of the calculated values of electrical conductivities

Figure 2: Experimental setup: (a) platinum electrodes; (b) Pt–PtRh thermocouple; (c) plug fitting (vacuum rubber); (d) nickel screens; (e) alundum tubes; (f) boron nitride bar; (g) glassy carbon crucible; (h) electrolyte under study; and (i) tube for evacuation and gas feeding.

Figure 3: IR transmission spectra of frozen \(\alpha\)-Al\(_2\)O\(_3\)/(Li\(_2\)CO\(_3\)–Na\(_2\)CO\(_3\)–K\(_2\)CO\(_3\))\(_{\text{eut}}\) samples taken from the bottom and upper parts of the oxide-salt composite.

Figure 4: Temperature dependence of the electric conductivity for the system: (Li\(_2\)CO\(_3\)–Na\(_2\)CO\(_3\)–K\(_2\)CO\(_3\))\(_{\text{eut}}\). (a) Literature data [12]; (b) experimental data (circles); (c) \(\alpha\)-Al\(_2\)O\(_3\) (20 wt%)/0.72(Li\(_2\)CO\(_3\)–Na\(_2\)CO\(_3\)–K\(_2\)CO\(_3\))\(_{\text{eut}}\) (squares); (d) \(\alpha\)-Al\(_2\)O\(_3\) (40 wt%)/0.72(Li\(_2\)CO\(_3\)–Na\(_2\)CO\(_3\)–K\(_2\)CO\(_3\))\(_{\text{eut}}\) (triangles); the data calculated with (2) are indicated by dotted lines.
from the experimental data does not exceed 5%. Therefore, the decrease in conductivity of the molten carbonate eutectic upon its thickening with the non-conductive \( \alpha \)-Al\(_2\)O\(_3\) powder is due to the reduction of charge carriers per volume unit of the electrolyte.

Isotherms of the specific conductivity of the thickened carbonate eutectic (Fig. 5) demonstrate that the specific conductivity of the suspension linearly decreases with the increasing dispersed particles content.

The experimental data of the \( \alpha \)-Al\(_2\)O\(_3\)/(Li\(_2\)CO\(_3\)–Na\(_2\)CO\(_3\)–K\(_2\)CO\(_3\))\(_{\text{eut}}\) system conductivity may be approximated by (4) with a confidence coefficient 0.99. The regression equation is valid in the interval from 0 to 40 wt% of the dispersed \( \alpha \)-Al\(_2\)O\(_3\) content and in the temperature range from 680 K to 800 K.

\[
\ln \sigma = 4.007 - 3406/T - 0.00197 \cdot c(\text{Al}_2\text{O}_3)^{1/2}
\]  

(4)

Here \( \sigma \) is the electrical conductivity (S/cm), \( T \) is the temperature (K) and \( c(\text{Al}_2\text{O}_3) \) is the concentration of \( \alpha \)-Al\(_2\)O\(_3\) (wt%). The discrepancy in specific conductivity between the experimental and the calculated by (4) values does not exceed 5.5%. The average deviation is equal to 1%.

The temperature dependence of the specific conductivity of the molten carbonate–chloride mixture 0.72(Li\(_2\)CO\(_3\)–Na\(_2\)CO\(_3\)–K\(_2\)CO\(_3\))\(_{\text{eut}}\)–0.28NaCl is shown in Figure 6 (curve 1). Hence, it is obvious that addition of sodium chloride to the molten carbonate eutectic increases the electrical conductivity of the melt. For the thickened system, containing 40 wt% of the fine \( \alpha \)-Al\(_2\)O\(_3\) powder, specific conductivity is lower than that for the \( \alpha \)-Al\(_2\)O\(_3\)/(Li\(_2\)CO\(_3\)–Na\(_2\)CO\(_3\)–K\(_2\)CO\(_3\))\(_{\text{eut}}\) system (curve 2). The temperature dependences of the specific conductivity of the molten 0.72(Li\(_2\)CO\(_3\)–Na\(_2\)CO\(_3\)–K\(_2\)CO\(_3\))\(_{\text{eut}}\)–0.28NaCl mixture and of the \( \alpha \)-Al\(_2\)O\(_3\)/(Li\(_2\)CO\(_3\)–Na\(_2\)CO\(_3\)–K\(_2\)CO\(_3\))\(_{\text{eut}}\)–0.28NaCl system may be approximated by the second-order polynomials (Table 1).

<table>
<thead>
<tr>
<th>( \alpha )-Al(_2)O(_3) (wt%)</th>
<th>( A ) (S/cm)</th>
<th>( B_1 ) (S/(cmK)) ( 10^2 )</th>
<th>( B_2 ) (S/(cmK(^2))) ( 10^5 )</th>
<th>( \sigma \pm \Delta \sigma ) at 773 K (S/cm)</th>
<th>( R^2 )</th>
<th>( n )</th>
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</thead>
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<tr>
<td>0</td>
<td>-0.4668</td>
<td>-0.990</td>
<td>0</td>
<td>0.3199</td>
<td>0.68 ± 0.01</td>
<td>0.99</td>
</tr>
<tr>
<td>20</td>
<td>-2.099</td>
<td>0.345</td>
<td>0</td>
<td>0</td>
<td>0.57 ± 0.01</td>
<td>0.99</td>
</tr>
<tr>
<td>40</td>
<td>-0.165</td>
<td>0.205</td>
<td>0</td>
<td>0</td>
<td>0.42 ± 0.01</td>
<td>0.99</td>
</tr>
<tr>
<td>( \alpha )-Al(_2)O(_3)/(Li(_2)CO(_3)–Na(_2)CO(_3)–K(_2)CO(<em>3))(</em>{\text{eut}})–0.28NaCl</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>0</td>
<td>5.6952</td>
<td>-1.696</td>
<td>1.3872</td>
<td>0.87 ± 0.01</td>
<td>0.99</td>
<td>130</td>
</tr>
<tr>
<td>40</td>
<td>6.6249</td>
<td>-1.929</td>
<td>1.4331</td>
<td>0.28 ± 0.01</td>
<td>0.99</td>
<td>109</td>
</tr>
</tbody>
</table>

As shown in our previous study [10] XRD analysis of the solidified carbonate–chloride melt thickened with powdered \( \alpha \)-Al\(_2\)O\(_3\) showed the presence of Li\(_2\)CO\(_3\), Na\(_2\)CO\(_3\), K\(_2\)CO\(_3\), NaCl and \( \alpha \)-Al\(_2\)O\(_3\) phases. The synchronous thermal analysis and Raman spectroscopy data also confirm the inertness of \( \alpha \)-Al\(_2\)O\(_3\) in carbonate–chloride melts at
temperatures ranging from 673 K to 793 K. Therefore, the formation of the additional non-conductive phases has not been observed in this system.

In this regard, the significant decrease in conductivity of the carbonate–chloride melt that coexisted with the finely dispersed $\alpha$-Al$_2$O$_3$ is not sufficiently clear enough. It may be due to the adsorption of ions on the developed surface of the solid particles [3]. This phenomenon will complicate the process of charge transfer in composite electrolytes.

4 Conclusion

The specific electrical conductivity of composite electrolytes: $\alpha$-Al$_2$O$_3$/(Li$_2$CO$_3$–Na$_2$CO$_3$–K$_2$CO$_3$)$_{eut}$ and $\alpha$-Al$_2$O$_3$/(Li$_2$CO$_3$–Na$_2$CO$_3$–K$_2$CO$_3$)$_{eut}$–0.28NaCl with the aluminium oxide content up to 40 wt% was investigated.

It was revealed that the electrical conductivities of carbonate and carbonate–chloride electrolytes have been changed differently when thickened with $\alpha$-Al$_2$O$_3$ powder.

The obtained data testified that the effective electrical conductivity of $\alpha$-Al$_2$O$_3$/(Li$_2$CO$_3$–Na$_2$CO$_3$–K$_2$CO$_3$)$_{eut}$ system containing 0–40 wt% of aluminium oxide could be uniquely determined by the liquid phase conductivity. Whereas for carbonate–chloride melts, the reduction of the specific electric conductivity upon thickening of $\alpha$-Al$_2$O$_3$ is much greater than the effect associated with a decrease in the volume concentration of charge carriers.

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References