Influences of Temperature on the Conductive Properties of Single Crystal C12A7: e⁻

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C12A7 single crystals were grown by CZ method in 2% oxygen containing N₂ atmosphere. C12A7: e⁻ single crystals were gotten by metal reduction method. Nyquist diagrams for C12A7: e⁻ single crystals under different temperatures in 3.5 wt% NaCl solution were tested. Results show that electrical conductivity of C12A7: e⁻ decreased when the temperature was increased due to the lattice scattering of electrons and defects in the C12A7: e⁻ single crystals. Corrosion resistance of the C12A7: e⁻ single crystal was decreased compared with C12A7 crystal, which decreased evidently as the temperature increase.

Keywords: C12A7: e⁻ single crystals; Electrical conductivity; Corrosion resistance; potentiodynamic polarization;

1. INTRODUCTION

C12A7 crystal is a semiconductor co-existence of transparency and conductivity with a lattice framework composed of nano-size cage structure [1]. Its chemical formula is 12CaO•7Al₂O₃ (C12A7) belongs to the cubic space group I43d with a lattice constant of 1.199 nm [2]. The unit cell is composed of a positively charged [Ca₂₄Al₂₈O₆₄]⁴⁺ lattice framework that contains 12 sub-nanometer-size cages [1, 2]. To compensate for the positive charge of the lattice framework, two O²⁻ ions are accommodated in a unit cell. The feature is zeolite-like one, in which oxide ions (O²⁻) are trapped in a Ca-Al-O cage in the stochimometric composition. C12A7 is known as an oxygen ionic conductor which can be replaced by various anions such H⁺, Cl⁻, e⁻, to construct a new material such as semiconductor, cold electron-emitting material and catalytic [3-7]. These materials were called ionic
compound or organic electrides [8]. C12A7 crystal is environmental friendly material for LED with abundant reserves [9].

As mentioned in the previous section, when a low concentration of electrons is trapped at anion vacancies, $F^+$ centers are generated. Crystalline electrides can be seen as stoichiometric $F$-centers in which all ionic sites contain trapped electrons [10, 11, 12]. J. Dye defined these materials as compounds where the electrons behave as anions populating sites normally occupied by $\text{Cl}^-$ and $\text{OH}^-$. According to his definition they are neither delocalized as in a metal, nor localized on specific atoms or molecules. Electrides are strongly reducing materials where the electrons are localized in cavities at separatesites from the cations. They are well defined crystalline salts, whose crystal structure can be determined. The mobility of the trapped electrons depends on the structure and is apparently influenced by the size and length of the cavities or channels that connect the different anionic sites. Prior to the work on mayenite, all electrides made to date are organic and the key to their synthesis is the capture of the cation in an alkali metal solution by a non-reducible complexant, usually a crown ether, a cryptand or their nitrogenous analogs. The thermal instability combined with the difficulty to grow large samples of these compounds has been the major impediment to study their properties. Little is know about their electrical properties and the relationship to the crystal structure [10].

2. EXPERIMENTAL

2.1. Preparation C12A7 single crystals

Stoichiometric mixtures of both 99.99% pure $\text{CaCO}_3$ and $\text{Al}_2\text{O}_3$ were used as the starting materials. The mixture was synthesized in 100% oxygen atmosphere for 6 hours and the Synthesis temperature was 1200°C. The prepared material was put into the iridium crucible and induction-heated to melt at a controlled temperature, afterwards, the temperature turned to 1390°C in order to crystallize C12A7 single crystal, seed for the first time was Pt silk and the gotten piece of crystal was used for the seed in the following process. The crystal was slowly pulled up from the melt at a rate of 1.0-1.5 mm/h with a seed rotation rate of 10-20 rad/min. After completion of the grown process, the grown crystal was gradually cooled to room temperature in 20-50 h to avoid cracks caused by thermal stress.

Large single crystals were vacuum sealed in silica glass tubes in the presence of Ti shot and heated to 1300°C for 100 hours. Once out of the silica tubes, the samples presented a surface layer of crystalline TiO that was mechanically removed to expose the now reduced $\text{Ca}^{12}\text{Al}^{14}\text{O}_{33}$ crystal. The reaction can be written as function of the treatment time. X-ray measurements revealed that the treatment did not change the basic structure of the framework.

$$\left[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}\right]^{4+} + 2O^{2-} + Ti = TiO + \left[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}\right]^{4+} + (2-x)O^{2-} + (2x)e^-$$

(1)

2.2. Analysis of composition and structure of PEO coatings

The phase composition of the gotten crystal was investigated by means of power X-ray diffraction (XRD), using a Cu Ka source. Electrochemical impedance spectroscopy (EIS) and
potentiodynamic polarization experiments were performed through Princeton-4000 electrochemical analyzer. EIS was used to analyze the drift resistance in C12A7: e⁻ single crystals under different temperature during immersion in 3.5% NaCl solution. Each sample was mounted by paraffin with 1cm² surface exposed. The signal amplitude of EIS was 10 mV over frequency ranged between 0.01 and 100 kHz.

All electrochemical measurements were performed with a conventional three electrodes system of samples as working electrode, a platinum plate as auxiliary electrode and Ag/AgCl(sat KCl) as reference electrode.

3. CORROSION BEHAVIOR OF THE C12A7: E- SINGLE CRYSTALS UNDER DIFFERENT TEMPERATURES

3.1 Electrochemical impedance spectroscopy characteristics

Fig 1 was the XRD partten of power of C12A7 single crystal and C12A7: e⁻ single crystal. Although sample C12A7: e⁻ were gotten by metal reduction method, no other peaks except for C12A7 phase occurs in this diagram and it means the lattice structure of C12A7: e⁻ single crystal was not changed. Electrons in C12A7: e⁻ single crystal located at O²⁻ lattice site instead of interstitial site.

![Figure 1. XRD patterns of the C12A7 crystal and C12A7: e⁻ crystal](image)

The EIS characteristics of C12A7: e⁻ samples were measured in 3.5% NaCl solution under different temperatures. EIS equivalent circuit for C12A7: e⁻ sample tested under different temperatures was proposed as shown in Fig.2, in which the temperature is 30°C, 70°C and 80°C, respectively.
From the equivalent circuit, the impedance of the measured system between reference electrode (Ag/AgCl(sat KCl)) and working electrode (C12A7:e⁻) consisted of three parts: electrolyte, C12A7:e⁻ and Silver conductive adhesive. Resistance of C12A7: e⁻ single crystals were divided into three parts due to the different translational speed of current carrier on the outer layer and the inner layer. The solution resistance ($R_s$), the interface resistance ($R_p$) and the drift resistance ($R_b$) of the C12A7: e⁻ in parallel with $Q_b$. the capacity element is expressed as follows,

$$Z_{CPE}=1/[T(j\omega)^n]$$

(2)

In which $T$ is the admittance constant, $j$ is imaginary number, $\omega$ is the angular frequency, and $n$ is the exponent ranging between 0 and 1. The case $n = 1$ describes an ideal capacitor while the case $n = 0$ describes a pure resistor. While the value of 0.5 implied that the circuit reflected the Warburg impedance. With the Nyquist plots based on the equivalent circuit model shown in Fig. 3, an excellent fit was made between the experimental data and iterated result.

**Figure 2.** Nyquist diagrams for C12A : e⁻ under different temperatures in 3.5 wt% NaCl solution

**Figure 3.** Equivalent circuit related to the EIS plots of the C12A7: e⁻ obtained by different current density
The results of the fitting parameters for simulative EIS spectra of the C12A7: e⁻ samples obtained under different temperatures were shown in Table 1. It could draw conclusions from the EIS results that the drift resistance of C12A7: e⁻ single crystal was increased evidently by 2-3 orders after the temperature increased due to the suppressed of carrier movement. The different EIS behavior (corrosion resistance) of the C12A7 single crystal could be due to their movement of defects and electrons. As temperature was increased, the translational speed of defects and electrons changed little. But lattice scattering was enhanced.

<table>
<thead>
<tr>
<th>Sample (A/dm²)</th>
<th>Rs (Ω)</th>
<th>Qp⁻Y₀ (Ω⁻¹ s⁻¹ cm²)</th>
<th>n_p</th>
<th>R_p (Ω)</th>
<th>Qb⁻Y₀ (Ω⁻¹ s⁻¹ cm²)</th>
<th>n_b</th>
<th>R_b (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30°C</td>
<td>24.61</td>
<td>1.496E-6</td>
<td>0.9163</td>
<td>1017</td>
<td>0.0001234</td>
<td>0.2963</td>
<td>9882</td>
</tr>
<tr>
<td>70°C</td>
<td>15.38</td>
<td>9.174E-8</td>
<td>0.9463</td>
<td>2.0E4</td>
<td>0.0001463</td>
<td>0.8</td>
<td>8907</td>
</tr>
<tr>
<td>80°C</td>
<td>14.12</td>
<td>0.0002856</td>
<td>0.1244</td>
<td>2.6E7</td>
<td>0.9939</td>
<td>0.6267</td>
<td>2.6E4</td>
</tr>
</tbody>
</table>

From table 1 Rs was solution resistance which was changed little with temperatures. Rp and Rb were the interface resistance and drift resistance in C12A7: e⁻ single crystal. Rb and Rp were determined by the carrier density and mobility of carriers. Carrier density changed little with temperatures[13]. When the temperature increased the mobility of defects and electrons was suppressed by the lattice scattering. So the resistance of C12A7: e⁻ single crystals were increased[14,15].

### 3.2 Potentiodynamic polarization

The potentiodynamic polarization curves of C12A7: e⁻ in 3.5% NaCl solution under different temperatures are shown in Fig. 4 and the associated electrochemical data are listed in Table 2.

These data clearly show that the corrosion resistances of these samples C12A7: e⁻ under different temperatures were evidently different. Speed of the corrosion was increased from 30°C to 80°C, surface of the C12A7: crystal turn to rude, optically corrosion occurred, the C12A7: Corrosion current Density was 43.448 nA under 30°C, Corrosion current Density was 8.742 µA under 80°C. C12A7 was insoluble in nitric acid and hydrochloric acid. It is hard to soluble in NaCl solution, but...
C12A7: e\(^{-}\) was easy to dissolve in NaCl solution the same as metal. It is another kind of organic electrides.

![Figure 4](image)

**Figure 4.** Potentiodynamic polarization curves of samples with different current density in the 3.5 wt% NaCl solution.

**Table 2.** Corrosion current Density and Corrosion Potential of C12A7: e\(^{-}\) under different temperatures

<table>
<thead>
<tr>
<th>(temperature)</th>
<th>Icorr</th>
<th>Ecorr</th>
<th>Ba</th>
<th>Bc</th>
</tr>
</thead>
<tbody>
<tr>
<td>30(^{\circ})C</td>
<td>43.448 nA</td>
<td>-894.962 mV</td>
<td>314.337 mV</td>
<td>265.373 mV</td>
</tr>
<tr>
<td>80(^{\circ})C</td>
<td>8.742 µA</td>
<td>118.475 mV</td>
<td>239.683 mV</td>
<td>168.641 mV</td>
</tr>
</tbody>
</table>

**4. CONCLUSION**

Electrochemical properties of C12A7: e\(^{-}\) single crystal under different temperatures was studied in this paper. And the electrical conductivity changed with the temperatures which was caused by lattice scattering of carriers. Corrosion resistance of the C12A7: e\(^{-}\) single crystal was decreased compared with C12A7 crystal, corrosion current of C12A7: e\(^{-}\) was 43.448 nA under 30\(^{\circ}\)C, corrosion current of C12A7: e\(^{-}\) was 8.742 µA under 80\(^{\circ}\)C, electrons and defects increased with the temperatures and corrosion of C12A7: e\(^{-}\) single crystal were enhanced

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References


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