Anodic dissolution of gallium in alkali metal chloride melts

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Abstract

Gallium and gallium based alloys can be potentially used in pyrochemical and pyroelectrochemical reprocessing of spent nuclear fuels, particularly for separating actinides and rare earth fission products. However, the electrochemical behavior of gallium in high temperature molten salt electrolytes is very little studied. The present work was aimed at investigating the processes taking place during anodic dissolution of gallium in fused alkali chlorides (the ternary 6NaCl–9KCl–5CsCl eutectic mixture) and determining the ratio of gallium chloro-species in different oxidation states formed and remained in the melt. The experiments were performed between 550 and 750 °C, and the anodic current density varied from 0.024 to 0.094 A/cm². Anodic polarization and coulometry were used, and the results obtained demonstrated that two gallium species, Ga(I) and Ga(III), were formed as a result of gallium anodic dissolution. The ratio between these two oxidation states depended on temperature and anodic current density. The method of processing the experimental data and the calculated values of the ratio of gallium ionic forms in the system under various conditions are presented.

Keywords
anodic dissolution
gallium
chloride melts
gallium chlorides
anodic polarization

1. Introduction

Appeal and economic feasibility of nuclear power can be increased by switching from the current open to a closed nuclear fuel cycle, enabling more efficient use of fissile materials. This approach involves reprocessing spent nuclear fuel (SNF) with re-use of unspent uranium and newly formed fissile materials, including plutonium. Separation of nuclear fuel components with subsequent refabrication allows reducing the demand for freshly mined uranium and, at the same time, minimizing the amount of radioactive substances that otherwise would be sent to disposal [1].

It is interesting to note that the closed nuclear fuel cycle may be one of the key aspects of the transition to more sustainable and environmentally friendly nuclear power generation since the use of fissile materials in the closed cycle allows producing much more energy from the same amount of uranium than in the traditional open cycle. Moreover, reprocessing of spent nuclear fuel can be supplemented with innovative technologies, such as extraction of rare or noble metals present as fission products or production of isotopes for medical or technical use, which can significantly improve the economic efficiency of this process. To date, the most common method of industrial reprocessing of SNF is the solvent extraction (PUREX) process [1]. However, despite its effectiveness, this method has a number of disadvantages including a long SNF holding time after unloading from the reactor before sending for
reprocessing. Susceptibility of water and organic solvents to radiolysis requires cooling SNF for at least 3 years; in practice this period is often extended to 7–10 years. To improve economics of the reprocessing it is necessary to shorten the SNF cooling time before reprocessing to 6 months, moving from a closed to a short closed nuclear fuel cycle. However, when this requirement is met, the SNF retains a very high specific activity (about 10^19 Bq/t). Thus, the economic necessity of the transition from the ordinary closed nuclear fuel cycle to the short closed nuclear fuel cycle does not allow relying on the traditional aqueous reprocessing methods.

One of the alternative approaches to SNF processing is the use of non-aqueous processes, including processes in which molten salts or metals act as working media. These media have a very high radiation resistance and do not contain neutron moderators, allowing handling SNF after short cooling time and working with systems that are very concentrated in fissile materials. Various classes of inorganic salts were considered as the solvents in non-aqueous reprocessing technologies [2–4], including chlorides and fluorides [5–10], nitrates [11], sulfates [12], carbonates [13], molybdates and tungstates [8]. So far, processes based of fused chlorides are the most developed and close to a medium or large-scale implementation.

A promising method of SNF processing based on non-aqueous processes and allowing more complete extraction of valuable components from spent nuclear fuel is the selection of SNF components in the “molten salt – liquid metal (alloy)” system. This method of separation of components is carried out using the exchange redox reactions (reductive extraction) or when an external potential is applied (by electrolysis). Electrolysis is more commonly considered approach, and the working medium (liquid metal or alloy) in this case makes an electrode. One of the preferred liquid metal electrodes is gallium or a gallium-based alloy [14, 15].

Developing a feasible reprocessing technology requires comprehensive and reliable information about the electrochemical properties of all elements involved in the process. In recent years behavior of f-elements in gallium-containing alloys in relation to SNF reprocessing attracted considerable attention [15–18]. Electrochemical and thermodynamic properties of uranium [19–24] and various rare earth metals representing fission products [19–23, 25–32] were extensively investigated in various gallium-containing alloys. Apart from pure gallium [14, 15, 24, 31, 32], alloys based on gallium–indium [14, 19–21, 23, 25, 26, 29], gallium–aluminum [14, 22, 23, 30], gallium–tin [14] and gallium–zinc [14, 27] mixtures of eutectic and non-eutectic compositions were considered. Electrochemical and thermodynamic properties were then used to calculate possible actinide and lanthanide separation factors [15, 28, 33], which subsequently received experimental verification [34].

Although the electrochemistry of solutes (uranium and lanthanides) is currently well understood, considerably less attention was paid to the electrochemical properties and behavior of the solvents (gallium and gallium-based alloys). Surprisingly, the electrochemistry of gallium in fused alkali chlorides was very little investigated. The difficulty of studying its electrochemical behavior in molten chloride electrolytes is determined by the fact that gallium ions in two oxidation states are concurrently present in the melt in the equilibrium with the metal. Therefore, three redox couples can exist simultaneously in the system, i.e., Ga/Ga^3+, Ga/Ga^3+, Ga^+/Ga^3+. Pioneering studies on gallium electrochemistry in alkali chloride melts involved determination of gallium electrode and redox potentials in 3LiCl–2KCl eutectic [35]. The authors [35] reported the presence of two types of gallium ions (Ga^+ and Ga^3+) in the electrolyte held in contact with metallic gallium. Subsequent studies performed in other molten chloride mixtures confirmed those findings [36].

Additional information concerning the oxidation state of metal ions stable in molten electrolytes can be gained from studying the process of anodic dissolution of the corresponding metal. Apart from its importance for the fundamental science, anodic dissolution is one of the options for separating actinides or fission products (e.g. rare earths) from liquid metal based alloys. Although the difference in the electrode potentials of gallium and f-elements should be sufficient for performing such separation, understanding the anodic behavior of all components forming the electrode (anode) is nevertheless essential for organizing the efficient process. Repeated use of gallium alloys as electrodes would inevitably result in gradual accumulation of impurities (e.g., intermetallic compounds, which are more electropositive than the corresponding metals), and gallium can be in turn reprocessed by electrowinning to concentrate impurities and return the metal back into the SNF reprocessing technology. Performing gallium refining, again, relies on understanding the metal’s anodic behavior.

Available literature contains no information concerning anodic dissolution of gallium in chloride melts. The present work was therefore aimed at studying the process of anodic dissolution of gallium in alkali chloride-based melts and determining the ratio of various valence forms of gallium present in the melt. The eutectic mixture of sodium, potassium and cesium chlorides, 6NaCl–9KCl–5CsCl, was chosen as the molten chloride electrolyte, owing to its interest for practical use in pyrochemical technologies of SNF processing.

Amongst the possible candidate electrolytes for pyrochemical reprocessing of spent nuclear fuels, the binary eutectic mixture of lithium and potassium chloride received the most attention. This mixture has low melting point and is relatively inexpensive. The main disadvantage of 3LiCl–2KCl mixture is hygroscopicity (due to presence of LiCl). The ternary 6NaCl–9KCl–5CsCl mixture is non-hygroscopic and low-melting, albeit more expensive. The presence of cesium cations increases stability of the transition metal complex ions present in the melt in contrast with the strong polarizing effect from small lithium cations in 3LiCl–2KCl melts. All
advantages and disadvantages of potential fused chloride electrolytes still need to be assessed.

2. Experimental

The experiments were conducted in the melts based on the ternary 6NaCl–9KCl–5CsCl (30 mol.% NaCl, 24.5 mol.% KCl, m.p. 480 °C) eutectic mixtures. The mixture of the required composition was prepared by fusing individual sodium, potassium and cesium chlorides. Individual alkali chlorides, additionally purified prior to the experiments as described previously [37], were mixed in the required proportion, loaded in to a silica cell and fused under vacuum at 750 °C. After a homogeneous melt was formed, the temperature was lowered to 600 °C and the melt was sparged with gaseous hydrogen chloride for three hours to convert all oxygen containing impurities possible present in the salts to chlorides. Molten salt was then poured into alumina crucibles, cooled in a desiccator and stored in argon filled glove box (Glovebox Systemtechnik GmbH, <5 ppm % O<sub>2</sub>, <0.1 ppm H<sub>2</sub>O).

All the experiments were conducted under argon (99.998%) atmosphere. The electrochemical measurements were performed using an AUTOLAB PG302N potentiostat/galvanostat.

The anodic dissolution experiments were carried out in an electrochemical cell with two electrodes schematically shown in Figure 1. Gallium served as the working electrode (anode). The surface area of gallium electrode was 1.06 cm<sup>2</sup>. Tungsten wire was used as the current conductor to metallic gallium. Sides of the wire were insulated from the contact with molten salt electrolyte by a ceramic tube. The mass of metallic gallium was determined before and after the experiment. Counter electrode (cathode) consisted of a silica sheath (with a diaphragm in the bottom) containing (6NaCl–9KCl–5CsCl)–PbCl<sub>2</sub> electrolyte and a molybdenum wire dipped into this electrolyte. The cathodic reaction therefore involved reduction of Pb<sup>2+</sup>ions to metallic lead.

The experiments involved the quantitative measurement of the mass of metallic gallium before and after the passage of current through the system. The amount of electric charge passed through the system in all experiments was 600 C. Anodic dissolution was run in a galvanostatic mode at constant current values of 0.025, 0.05, 0.075 and 0.1 A (corresponding to the current densities of 0.024, 0.047, 0.071 and 0.094 A/cm<sup>2</sup>) in the temperature range of 550–750 °C. At such low current densities (below 0.1 A/cm<sup>2</sup>) the current efficiency was taken as quantitative.

After completing anodic dissolution, a sample of the molten chloride electrolyte was syringed into a silica tube and used for subsequent chemical analysis to determine concentration of gallium ions in the salt melt. The experimental cell was then lifted from the furnace and cooled as quickly as possible using a fan (in order to minimize the effect of possible reactions taking place in the electrolyte). The entire content of the main crucible (8 in Figure 1) was then treated with distilled water to dissolve chloride salts. All metallic gallium remaining in the crucible was collected, thoroughly washed with distilled water and then with acetone. Then gallium was transferred to a preliminary weighted vessel, left at the room temperature until all acetone evaporated (i.e., until two consequent weightings showed no weight decrease) and weighted.

Quenched salt in the capillary tube taken for analysis was thoroughly grinded in a mortar, and then samples of it were weighted, transferred to volumetric flasks and dissolved in 5 ml of 1 M solution of hydrochloric acid. After the salts dissolved the solution was diluted with distilled water. Aliquots of these solutions were then taken and diluted to bring the total concentration of salts below 0.001 g/ml. Gallium concentration in the solutions was then determined using inductively coupled plasma atomic emission spectroscopy (Optima 2100 DV spectrometer, Perkin Elmer).

Measurements of anode polarization were also carried out using the experimental cell shown in Figure 1. Gallium anode was polarized at a constant current value for 30 s. This followed a 90 s period with the polarizing current switched off. Polarizing current value was gradually increased from 0.0001 to 1 F. A potential of the anode recorded 0.1 s after switching the polarizing current off was used for plotting the polarization curve.

![Figure 1](image-url)  
**Figure 1** Scheme of the electrochemical cell for anodic dissolution.  
1 – silica sampling tube; 2 – vacuum rubber stopper; 3 – outer silica cell; 4 – silica sheath of reference electrode; 5 – molybdenum wire; 6 – melt in the reference electrode sheath (6NaCl–9KCl–5CsCl + PbCl<sub>2</sub>); 7 – reference electrode diaphragm; 8 – crucible; 9 – gallium metal in a small beryllium oxide crucible; 10 – insulating ceramic tube; 11 – tungsten wire; 12 – beryllium oxide thermocouple sheath.
3. Results and Discussion

An example of the anodic polarization curve obtained for gallium electrode in the ternary 6NaCl–9KCl–5CsCl eutectic melt is presented in Figure 2. Increasing anodic current density shifted the potential of the electrode to more positive values. The polarization curve includes two rising sections separated by approximately 0.2 V at the potentials around –(0.55–0.50) and –(0.36–0.28) V. Such behavior agrees well with the results of cyclic voltammetry measurements [36], and the rising parts on the polarization curve can be reasonably assigned to two electrochemical processes taking place at close potential values, i.e., Ga/Ga³⁺ and Ga/Ga⁺. Therefore, it can be expected that anodic dissolution of gallium would result in formation of two gallium species in the electrolyte, Ga(I) and Ga(III).

This assumption was confirmed by the results of anodic dissolution experiments. The number of electrons involved in the electrochemical anodic process was calculated from the experimentally determined mass decrease of the gallium anode using Faraday’s law:

\[
n = \frac{Q}{\vartheta \cdot F} = \frac{Q \cdot M}{\Delta m \cdot F} \tag{1}
\]

where, \( n \) is the average number of electrons involved in all ongoing electrochemical processes, \( Q \) is the amount of electricity passed through the system in experiment, \( \vartheta \) is the number of moles of dissolved gallium, \( F \) is the Faraday’s constant, \( M \) is the molar mass of gallium, and \( \Delta m \) is the mass of gallium dissolved during the experiment.

Taking into account that gallium ions in two oxidation states (Ga⁺ and Ga³⁺) are present simultaneously in the melt in equilibrium with the metal, the mean number of electrons can be expressed as:

\[
n = \frac{n(Ga^+) \cdot \vartheta(Ga^+) + n(Ga^{3+}) \cdot \vartheta(Ga^{3+})}{\vartheta} \tag{2}
\]

where, \( n \) is the average number of electrons involved in all ongoing electrochemical processes, \( n(Ga^+) \) is the number of electrons involved in the electrochemical process \( Ga \rightarrow Ga^+ \), \( n(Ga^{3+}) \) is the number of electrons involved in the electrochemical process \( Ga \rightarrow Ga^{3+} \), \( \vartheta(Ga^+) \) is the number of moles of Ga⁺ ions, \( \vartheta(Ga^{3+}) \) is the number of moles of Ga³⁺ ions, and \( \vartheta \) is the number of moles of dissolved gallium.

Because \( n(Ga^+) = 1 \) and \( n(Ga^{3+}) = 3 \), the following expression can be derived:

\[
n = \frac{\vartheta(Ga^+) + 3 \cdot \vartheta(Ga^{3+})}{\vartheta} = \varphi(Ga^+) + 3 \cdot \varphi(Ga^{3+}) \tag{3}
\]

where, \( \varphi(Ga^+) \) is the fraction of Ga⁺ ionic form in the total amount of gallium in the melt, \( \varphi(Ga^{3+}) \) is the fraction of Ga³⁺ ionic form in the total amount of gallium in the melt.

Since

\[
\varphi(Ga^+) = 1 - \varphi(Ga^{3+}) \tag{4}
\]

then

\[
n = 1 - \varphi(Ga^{3+}) + 3 \cdot \varphi(Ga^{3+}) = 1 + 2 \cdot \varphi(Ga^{3+}) \tag{5}
\]

\[
\varphi(Ga^{3+}) = \frac{n - 1}{2} \tag{6}
\]

Further, the ratio of gallium ionic forms obtained during the anodic dissolution process was calculated using Equation 6 and 4.

All experimental and calculated data are presented in Table 1. The results show that anodic dissolution of gallium results in formation in the melt of gallium ions in two oxidation states (Ga⁺ and Ga³⁺) in agreement with the results of the previous electrochemical measurements performed using stationary and transient methods [36, 37]. Therefore, there is a possibility of a disproportionation reaction taking place parallel to the reaction of anodic dissolution.

\[3Ga^+ \rightarrow Ga^{3+} + 2Ga. \tag{7}\]

The way by which the amount of gallium dissolved in the experiments was determined took into account the possible effect of this reaction since metallic gallium after completing the experimental runs was collected from the entire volume of the electrolyte. Therefore, the gallium weight decrease used in the subsequent calculations reflected the effect of disproportionation. Rapid cooling of the cell after the experiment minimized the effect of the disproportionation reaction after the anodic dissolution was finished. Therefore, the results obtained in the present study can be assumed to correspond to the processes taking place in the electrolyte in the course of anodic dissolution of gallium with the minimum effect from possible subsequent reactions.
Table 1 Experimental and calculated data on the anodic dissolution of gallium.

<table>
<thead>
<tr>
<th>$j$, A/cm$^2$</th>
<th>$T$, K</th>
<th>$m_{Ga_{0}}$, g</th>
<th>$m_{Ga_{final}}$, g</th>
<th>$\Delta m_{Ga}$, g</th>
<th>$n$ / ė</th>
<th>$\varphi(Ga^{3+})$, %</th>
<th>$\varphi(Ga^{+})$, %</th>
</tr>
</thead>
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<tr>
<td>0.024</td>
<td>809</td>
<td>3.2865</td>
<td>3.1272</td>
<td>0.1593</td>
<td>2.72</td>
<td>86</td>
<td>14</td>
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<tr>
<td></td>
<td>921</td>
<td>3.1346</td>
<td>2.8905</td>
<td>0.2441</td>
<td>1.78</td>
<td>39</td>
<td>61</td>
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<td></td>
<td>991</td>
<td>3.1318</td>
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<td>4.6</td>
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<td>2.9231</td>
<td>0.2202</td>
<td>1.97</td>
<td>48</td>
<td>52</td>
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<td></td>
<td>920</td>
<td>3.1987</td>
<td>2.9229</td>
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<tr>
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<td>3.6203</td>
<td>3.2183</td>
<td>0.402</td>
<td>1.08</td>
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<td></td>
<td>1001</td>
<td>3.7702</td>
<td>3.3477</td>
<td>0.4225</td>
<td>1.03</td>
<td>1</td>
<td>99</td>
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<tr>
<td>0.071</td>
<td>799</td>
<td>2.6415</td>
<td>2.3882</td>
<td>0.2533</td>
<td>1.71</td>
<td>36</td>
<td>64</td>
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<tr>
<td></td>
<td>898</td>
<td>2.7610</td>
<td>2.4824</td>
<td>0.2786</td>
<td>1.56</td>
<td>28</td>
<td>72</td>
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<tr>
<td></td>
<td>946</td>
<td>3.3584</td>
<td>3.0271</td>
<td>0.3313</td>
<td>1.31</td>
<td>15</td>
<td>85</td>
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<td></td>
<td>999</td>
<td>3.6475</td>
<td>3.1340</td>
<td>0.5135</td>
<td>0.84</td>
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<td></td>
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<tr>
<td>0.094</td>
<td>822</td>
<td>3.3518</td>
<td>3.1825</td>
<td>0.1693</td>
<td>2.56</td>
<td>78</td>
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<td>3.1939</td>
<td>0.4328</td>
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<td>100</td>
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For the experiments conducted at the current densities of 0.047, 0.071 and 0.094 A/cm$^2$, the final concentrations of gallium ions in the salt melt were measured using the method of atomic emission spectroscopy with inductively coupled plasma. The results of the analysis are presented in Table 2.

The average number of electrons involved in the anodic process was between one and three (Table 1) confirming that gallium ions in two oxidation states, i.e., $+1$ and $+3$, were formed during anodic dissolution of the metal.

Figure 3 shows that the number of electrons involved in the reaction decreases with an increase in temperature, the ionic form of Ga$^+$ becomes more favorable compared to Ga$^{3+}$, and the Ga/Ga$^{+}$ redox couple begins to prevail. Such effect of temperature reflects the different slopes of temperature dependences of formal standard electrode potentials of gallium. The slope of Ga$^{0}$/Ga$^{+}$ temperature dependence is higher than that of Ga$^{3+}$/Ga$^{+}$ [36].

Table 1 shows that the weight loss of metallic gallium ($\Delta m_{Ga}$) increased with temperature, although the total amount of electricity passed through the system was the same. Figure 4, however, shows that the total gallium content in the electrolyte decreased with temperature. Such apparent contradictory behavior is explained by partial evaporation of gallium chloride from the molten salt electrolyte.

Table 2 Final concentrations of gallium in the salt melt measured using the method of atomic emission spectroscopy with inductively coupled plasma.

<table>
<thead>
<tr>
<th>$j$, A/cm$^2$</th>
<th>$T$, K</th>
<th>$\omega$, wt.%</th>
</tr>
</thead>
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<tr>
<td>0.047</td>
<td>812</td>
<td>0.88</td>
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<td></td>
<td>920</td>
<td>0.62</td>
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<tr>
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<td>1001</td>
<td>0.15</td>
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<tr>
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<td>799</td>
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<td>898</td>
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<td></td>
<td>946</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>999</td>
<td>0.26</td>
</tr>
<tr>
<td>0.094</td>
<td>822</td>
<td>0.87</td>
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<tr>
<td></td>
<td>914</td>
<td>0.40</td>
</tr>
</tbody>
</table>

Figure 3 Dependence of the number of electrons participating in the reaction on temperature at different values of current density.

Figure 4 Dependence of the final concentration of gallium ions in the salt melt on temperature at different current densities.
Indeed, formation of a solid deposit on the inner walls of the upper cold part of the experimental cell was observed in the course of the experiments. Although chemical analysis of the sublimed substance was not performed, its formation can be taken as an indirect evidence of gallium chloride evaporation (and subsequent condensation) because the working temperatures were not sufficient to cause any significant evaporation of alkali chlorides, which have much higher boiling points and lower vapor pressure than gallium chlorides. It is likely that the vapor pressure of GaCl is higher than that of GaCl₃. Since increasing temperature favored the formation of gallium monochloride as the product of anodic dissolution (Table 1), the amount of gallium chloride evaporated from the melt would also increase with temperature, and the total concentration of gallium remaining in the electrolyte would decrease (Figure 4 and Table 2).

4. Limitations

Anodic dissolution of metals is one of the straightforward direct techniques for determining mean oxidation state of metal ions formed in the electrolyte. It produces consistent results when the electrochemical process is not accompanied by a chemical reaction (e.g., when ions in a single oxidation state are stable in contact with the metal). In case of gallium two types of ions are formed, Ga⁺ and Ga³⁺. Reaction of higher oxidation state ions (Ga³⁺) with the metal can, in principle, result in additional dissolution of gallium due to formation of monovalent Ga⁺. To assess such a possibility, it is necessary to perform continuous measurements after completing anodic dissolution to monitor gallium concentration in the electrolyte and evolution of the mean oxidation state of gallium species. This will be the aim of the following studies.

Performing similar studies in another melt of industrial importance (3LiCl–2KCl eutectic mixture) would also be of interest both from practical application (as the most favored electrolyte for pyrochemical SNF reprocessing) and fundamental points of view. The latter concerns assessing possible effect of the polarizing power of alkali cations (forming the second coordination sphere around gallium chloro-complex ions) on stability of gallium chloride complexes in fused alkali chlorides. Comparing two candidate melts would allow determining further advantages and disadvantages of different electrolytes as well as their suitability for technological application.

5. Conclusions

As a result of studying the process of anodic dissolution of gallium in 6NaCl–9KCl–5CsCl eutectic mixture, the fractions of Ga ions in various oxidation states transferred to the electrolyte were calculated. The results showed that increasing temperature led to decreasing the number of electrons participating in the reaction and, as a result, to lowering the mean oxidation state of gallium ions in the melt. This proves that with increasing temperature the ionic form of Ga⁺ becomes more favorable compared to the form of Ga³⁺, and the Ga/Ga⁺ process begins to prevail. Higher temperatures favor the formation of the lower oxidation state of gallium ions.

The subsequent chemical analysis of the final concentrations of gallium chlorides in the salt melt showed that with increasing temperature the amount of gallium dissolved with the given amount of electricity passed increased, while the concentration of gallium chlorides in the melt decreased. The results obtained confirmed the assumption about the predominant formation of Ga⁺ ions with increasing temperature and high volatility of gallium monochloride.

- **Supplementary materials**

  No supplementary materials are available.

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  Funding acquisition: V.A.V.
  Investigation: O.V.T., V.A.V.
  Methodology: O.V.T., V.A.V.
  Resources: V.A.V.
  Supervision: V.A.V.
  Visualization: O.V.T.
  Writing – original draft: O.V.T.
  Writing – review & editing: V.A.V.

- **Conflict of interest**

  The authors declare no conflict of interest.

- **Additional information**

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  Website:
References


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