Engineering compounds for the recovery of critical elements from slags: melt characteristics of Li$_5$AlO$_4$, LiAlO$_2$ and LiAl$_5$O$_8$

Sven Hampel,† lyad Alabd Alhafez,‡ Thomas Schirmer,¶ Nina Merkert,† Alena Schnickmann,¶ Haojie Li,§ Michael Fischlschweiger,§ and Ursula Elisabeth Adriane Fittschen*,†

*†Institute of Inorganic and Analytical Chemistry, Clausthal University of Technology, Clausthal-Zellerfeld, Germany
†Institute of Applied Mechanics, Clausthal University of Technology, Arnold-Sommerfeld-Straße 6, 38678 Clausthal-Zellerfeld, Germany
¶Institute for Repository Research, Clausthal University of Technology, Adolph-Roemer-Straße 2A, 38678 Clausthal-Zellerfeld, Germany
§Institute of Energy Process Engineering and Fuel Technology, Clausthal University of Technology, Agricolastraße 4, 38678 Clausthal-Zellerfeld, Germany

E-mail: ursula.fittschen@tu-clausthal.de
Phone: +49 (0)5323722205

Abstract

Engineered artificial minerals (EnAM) are core to a new concept of designing scavenger compounds for the recovery of critical elements from slags. It requires fundamental understanding of solidification from complex oxide melts. Ion diffusivity and
viscosity play a vital role in this process. In the melt, phase separations and ion transport give rise to gradients/increments in composition and with it to ion diffusivity, temperature and viscosity. Due to this complexity solidification phenomena are yet not well understood. If the melt is understood as increments of simple composition on a microscopic level, the properties of these are more easily accessible from models and experiments. Here we obtain this data for three stoichiometric lithium aluminum oxides. LiAlO$_2$ is a promising EnAM for the recovery of lithium from lithium-ion battery pyrometallurgical processing. It is obtained through the addition of aluminium to the recycling slag melt. The high temperature properties spanning from below to above the liquidus temperature of three stoichiometric Li-Al-Oxides: Li$_5$AlO$_4$, LiAlO$_2$, and LiAl$_5$O$_8$ are determined using molecular dynamic simulation. The compounds are also synthesised via the sol-gel route. The Li$^+$ ion exhibits the largest diffusivity. They are quite mobile already below the liquidus temperature, i.e. for LiAlO$_2$ at T = 1700 K the diffusion coefficient of the lithium ion equals $D = 3.0 \times 10^{-9}$ m$^2$ s$^{-1}$. The other ions Al$^{3+}$ and O$^{2-}$ do not move considerably at that temperature. The diffusivity of Li$^+$ is largest in the lithium-rich compound Li$_5$AlO$_4$ with $D = 32 \times 10^{-9}$ m$^2$ s$^{-1}$ at 2500 K. The viscosity is lower the higher the lithium content. The Li$_5$AlO$_4$ exhibits a viscosity of $\eta = 2.2$ mPa s at 1328 K which matches well with experimentally determined 2.5 mPa s at this temperature. The viscosity of LiAlO$_2$ at 1800 K is more than two times higher. These data sets can help to describe the melts on a microscopic level and understand how the melt properties will change due to gradients in the Li:Al concentration.

**Introduction**

**Recovery of critical materials from slags**

The recovery of critical materials from waste streams has become a major concern in industrialised regions of the world with limited primary resources. The European Union has
defined a list of materials critical for its economy and accessed their supply risk first time in 2011. It has been updating this list ever since. From the correlation of both, specific elements and materials were considered critical and of high priority for recycling efforts and prospecting. For example, heavy rare earth elements are considered very critical. With respect to increasing use of electric vehicles cobalt and recently lithium have been rated critical materials. Various pyrometallurgical routes have already been developed, e.g. by the company Umicore. As these routes only concentrate on the recovery of the more noble elements such as cobalt, nickel and copper, it is accepted that elements with high oxygen affinity (e.g. lithium, rare earth elements, tantalum) migrate into the slag. The maximum yield of lithium in the slag is reported to be > 80 wt. % of the total Li of the recycled batteries, although a substantial amount is lost through evaporation. Commonly, the slags are reused in construction work and the critical elements incorporated into them are lost for recovery. Leaching procedures are sometimes discussed. A new highly promising concept to facilitate a cost and resource efficient recovery is to bind these elements in minerals that can be easily separated and enriched from the slag. This new approach, which is currently being investigated in various research projects, is known as the "engineered artificial minerals" method. The term most often used to refer to these minerals is “engineered artificial minerals” (EnAM). The concept of the EnAM formation and liberation is illustrated in figure 1.

An efficient liberation and separation in general requires the EnAM to be the only/main compound formed from the melt bearing the critical element. Meaning, the ratio of the fraction of the element in the slag matrix (ElSM) to the fraction in the EnAm compound (ElEnAm) is minimized: ElSM/ElEnAm = min (optimum: 0). In the optimum case, the crystal morphology is isometric and the crystallite size is maximized, as small dendritic or needle-shaped crystals make liberation more difficult. If possible, an EnAm compound should be an early or first crystallizate, as this ensures that the crystals have sufficient space to grow and the target element cannot be incorporated into any other compound. Accordingly, it is
Figure 1: Concept of engineered artificial minerals

necessary to synthesize compounds from the melt that crystallize first at high temperatures and exhibit no competing phases.

Solidification of slags

The solidification from these complex melts is not well understood. Though the thermodynamic prediction of phase transitions is fundamental to understand compound formation, solidification from high temperature melts < 1000 °C is additionally governed kinetically.\textsuperscript{10} The viscosity of the melt and the individual ion diffusivity play a vital role in this process.\textsuperscript{11,12} In viscous melts, solidification may occur without the predicted crystal formation. High viscosity and low ion diffusivity can limit the support of constituent elements during crystal growth. The processes in the melt can be quite complex. During cooling, phase separation in the melt can occur in the form of liquid-liquid separations as well as solid-liquid separation.\textsuperscript{10,13,14} The phase separation give rise to composition gradients in solid-liquid separation and sharp compositional interfaces in liquid-liquid separation. Different composition translates into different viscosity, and melt-chemistry, \textit{e.g.,} redox-potential.\textsuperscript{15,16} Compounds like Fe$_2$O$_3$ reduce the viscosity significantly due to depolymerization of the silicate network.
and increase the oxygen diffusivity by an order of magnitude.\textsuperscript{17,18} As a first approximation, we propose to understand the melt as a regime of phase transitions with microscopic areas of simple composition. The description of those especially its viscosity and ion diffusivity will facilitate deeper understanding of the solidification.

**LiAlO\textsubscript{2} a potential EnAM for lithium recovery.**

The lithium aluminium oxide LiAlO\textsubscript{2} is an early crystallisate. It has been observed to form from silicate recycling melts when aluminium is added. It bound nearly all lithium and exhibited excellent characteristics for the subsequent crushing and sorting and hence was suggested as a potential EnAM for lithium recovery.\textsuperscript{5} High diffusivity of oxygen potentially increases the oxidation state of redox-active elements like manganese, which has a major influence on the formation of the EnAM LiAlO\textsubscript{2}.\textsuperscript{5,9} Accordingly, knowledge about the melt, e.g., diffusivity, and viscosity, has the potential to predict and design compound formation in metal oxide melts. Molecular dynamics (MD) simulations are a potent tool to study high temperature metal oxide properties. MD studies found that networks present in TiO\textsubscript{2}-FeO-Na\textsubscript{2}O melt significantly impact viscosity and solidification processes in slags.\textsuperscript{19} MD simulations of lithium aluminium oxides have been used to study the defect chemistry and sophisticated potentials could be developed due to the simple crystal structures and strong ionicity among ternary lithium-containing oxides.\textsuperscript{20,21} However, less attention was paid to transport properties such as viscosity. Here we study individual ion diffusity and viscosity of Li-Al-O-compounds with different Li:Al ratios according to their thermodynamically predicted phase diagram. These are important properties which help to understand microscopic conditions during solidification. The selected compounds differ in the Li:Al ratio, from lithium-rich to poor the compound stoichiometry is Li\textsubscript{5}AlO\textsubscript{4}, LiAlO\textsubscript{2}, and LiAl\textsubscript{5}O\textsubscript{8}. The unit cells of these compounds and the pure endmembers of Li\textsubscript{2}O and Al\textsubscript{2}O\textsubscript{3} are shown in figure 2. The diffusivity of Li\textsuperscript{+}, Al\textsuperscript{3+} and O\textsuperscript{2-} and viscosity at temperatures between 1000 - 1900 K were determined using MD simulation.
Figure 2: Crystal structure of the unit cell of (a) Li$_2$O, (b) Li$_5$AlO$_4$, (c) LiAlO$_2$, (d) LiAl$_5$O$_8$, and (e) Al$_2$O$_3$

Experimental and computational methods

Molecular Dynamic Simulations.

All the molecular dynamics simulations are performed with the open-source LAMMPS code.$^{22}$ Periodic boundary conditions are employed, and the time step in all the simulations is 1 fs. In the system Li$_2$O-Al$_2$O$_3$, three stable lithium aluminate compounds are studied: Li$_5$AlO$_4$, LiAlO$_2$ and LiAl$_5$O$_8$ beside Li$_2$O and Al$_2$O$_3$. In the present study, charged particles interact via the long range Coulomb potential supplemented by the short range Buckingham potential (equation 1):

$$V_{ij} = \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r_{ij}} + \left[ A_{ij} \exp \left( \frac{-r_{ij}}{\rho_{ij}} \right) - C_{ij} \frac{r_{ij}}{\rho_{ij}}^6 \right]$$  \hspace{1cm} (1)

Here $i$ and $j$ denote an interacting pair of two ions among lithium, aluminium, and oxygen separated by a distance $r_{ij}$, $\varepsilon_0$ stands for the dielectric constant. The Buckingham potential parameters are taken from Kuganathan et al.$^{20}$ and are listed in Table 1. Oxygen atoms polarizability is included using the core-shell model,$^{23}$ in which a harmonic spring connects the positive core (charge +0.8) with the negative shell (charge −2.8). The adiabatic core-shell model by Mitchell and Fincham$^{24}$ is used with the CORESHELL package within LAMMPS.
Table 1: Interatomic potential parameters used in the atomistic simulations of Li-Al-O systems using a core-shell model with $Y$ electrons and spring constant $K$

<table>
<thead>
<tr>
<th>Interaction</th>
<th>$A$ (eV)</th>
<th>$\rho$ (Å)</th>
<th>$C$ (eV Å$^6$)</th>
<th>$Y$ (e)</th>
<th>$K$ (eV Å$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^+-O^{2-}$</td>
<td>632.1018</td>
<td>0.2906</td>
<td>0.00</td>
<td>1.000</td>
<td>99999</td>
</tr>
<tr>
<td>Al$^{3+}-O^{2-}$</td>
<td>1109.92381</td>
<td>0.31540</td>
<td>0.00</td>
<td>3.00</td>
<td>99999</td>
</tr>
<tr>
<td>O$^{2-}-O^{2-}$</td>
<td>12420.5</td>
<td>0.2215</td>
<td>29.07</td>
<td>-2.80</td>
<td>31.0</td>
</tr>
</tbody>
</table>

Table 2: Compounds present in the Li$_2$O-Al$_2$O$_3$ system used in the simulations, their crystal systems, space groups, dimensions and the number of atoms. Initial atomic coordinates were taken from 26.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Crystal System</th>
<th>Space Group Symbol</th>
<th>Dimensions (Å)</th>
<th>Number of Atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$O</td>
<td>Cubic</td>
<td>Fm3m</td>
<td>56 $\times$ 56 $\times$ 56</td>
<td>20736</td>
</tr>
<tr>
<td>Li$_5$AlO$_4$</td>
<td>Orthorhombic</td>
<td>Pbc$a$</td>
<td>62 $\times$ 63 $\times$ 63</td>
<td>27440</td>
</tr>
<tr>
<td>LiAlO$_2$</td>
<td>Tetragonal</td>
<td>P4$_1$2$_1$2</td>
<td>57 $\times$ 57 $\times$ 69</td>
<td>21296</td>
</tr>
<tr>
<td>LiAl$_5$O$_8$</td>
<td>Cubic</td>
<td>P4$_3$32</td>
<td>71 $\times$ 71 $\times$ 71</td>
<td>40824</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>Trigonal</td>
<td>R3c</td>
<td>64 $\times$ 66 $\times$ 65</td>
<td>32380</td>
</tr>
</tbody>
</table>

The crystal structure of the five compounds at the initial state is summarized in Table 2 and shown in figure 2. Size effects of the simulated systems are expected to be small using properly large cells, and by applying periodic boundary conditions in all three dimensions. At first, the samples are relaxed at a temperature of around 300 K using an isothermal-isobaric (NPT) ensemble for 20 ps. After relaxation of the samples, the compounds are heated up to the target temperature which is dominantly 2500 K. This high temperature was chosen to ensure that all compounds are in liquid state. At the target temperature, the samples are relaxed again for 500 ps. All visualizations as well as the analysis of the radial distribution function and the coordination analysis are done by the software tool OVITO PRO. 25

**Calphad model.**

Calculation of Phase Diagram (CALPHAD) is a method that integrates experimental information, e.g., thermal and caloric material properties, phase diagram data as well as data from atomistic modelling to establish thermodynamic models and parameters such that the Gibbs energies for respective phases for various materials systems can be predicted. Applications
are for instance in the understanding of material’s microstructure and solidification predictions.\textsuperscript{27} Particularly, in terms of lithium-containing oxide material systems, CALPHAD is widely applied for calculating and predicting the phase diagrams and serves as input for non-equilibrium solidification modelling.\textsuperscript{7,28–33} In this work, thermodynamic models and thermodynamic database of the $\text{Li}_2\text{O}$-$\text{Al}_2\text{O}_3$ system are applied according to Konar \textit{et al.}\textsuperscript{33} Based on this, essential phase information is provided for synthesizing different lithium-containing samples.

**Chemicals.**

Lithium hydroxide, aluminium nitrate nona hydrate, citric acid, 65\% nitric acid, 25\% ammonia, 95-97\% sulfuric acid, and 35\% hydrogen peroxide were obtained in pro analysis quality from Carl Roth. Dilutions were performed with ultrapure water ($> 18.2 \Omega$ cm, Purelab Flex 4, ELGA Veolia).

Glazed porcelain crucibles (15 mL, wide form) were purchased from IDL for sintering of the powders. Crucibles were cleaned in boiling 10\% nitric acid for 4 h and were heated to 1000 °C for 2 h before usage.

Argon (99.996\% purity, Linde) was used for sintering in inert atmosphere.

**Instrumentation.**

Powder X-ray diffraction analysis (PXRD) was performed with a PANalytical X-Pert Pro diffractometer with $\text{Co K}_\alpha$ excitation (40 kV, 40 mA) as scatter sample in Bragg-Brentano geometry. Identification of the phases was evaluated with the PDF-2 ICDD database.\textsuperscript{34}

Sintering of the powders prepared by sol-gel-synthesis was performed in a Nabertherm L 3/11 furnace with minimal air supply. Preparation of $\text{Li}_5\text{AlO}_4$ took place in a Nabertherm LHT 02/18 furnace with automatic gas supply set to 200 L h$^{-1}$ argon at 1.2 bar. Heating ramps were set for both furnaces to 10 K min$^{-1}$, while cooling was limited by the furnace specifications. Microwave assisted digestions were performed in 10 mL quartz tubes in an
CEM Discover SP-D 80 microwave (300 W). Digestions were carried out in triplicates with about 25 mg of substance each using a mixture of 4 mL sulfuric acid and 0.5 mL hydrogen peroxide. The ramping temperature was set to 200 °C with 10 min ramping time and 20 min holding time. The digestion was repeated with additional 0.5 mL hydrogen peroxide added. The resulting solutions were diluted to a final volume of 25 mL for inductively coupled plasma optical emission spectrometry (ICP-OES).

ICP-OES was performed with a Varian Vista-MPX equipped with a vertical quartz torch (radial plasma) with a V-gap atomizer in a PTFE chamber. Torch power was set to 1.2 kW with 15 L min\(^{-1}\) argon for the plasma, 1.5 L min\(^{-1}\) argon around the torch as well as 0.88 L min\(^{-1}\) for the atomizer. Observation height was set to 12 mm with evaluation of lithium 670.78 nm and aluminium 396.15 nm lines.

Determination of the viscosity of Li\(_5\)AlO\(_4\) was obtained using a Hesse Instruments EM301 heating microscope. A 3 mm diameter cylinder of the compound with a height of 3 mm was heated to 400 °C using an 80 °C min\(^{-1}\) heating rate followed by 7 °C min\(^{-1}\) towards the maximum temperature of 1500 °C.\(^{35}\) The half sphere temperature was determined to be, 1055 °C. In another run, another cylinder of sample material was heated using the same rate as described before but with an end temperature of 1055 °C, which is held for 60 min. The heights and baseline of the shadow profile were used to calculate the squared half height width of the half of the profile. This value is plotted over the elapsed time, the obtained slope of 3097.1 \(\mu\)m\(^2\) s\(^{-1}\) of the linear regression R\(^2\) = 0.9439 was interpreted as diffusion coefficient D. The viscosity was then obtained using equation 3.

**Compound preparation.**

Synthesis of LiAlO\(_2\) and LiAl\(_5\)O\(_8\) was performed with a modified Pechini method similar to Blank *et al.*\(^{36}\) Lithium hydroxide and aluminium nitrate nona hydrate in corresponding mole fractions (total amount of substance = 30 mmol) were dissolved in about 30 mL of 20% nitric acid. Citric acid in 10mol% excess was added, and the mixture was set to a neutral
pH at reflux temperature with 25% ammonia solution. Excess water was evaporated upon self-ignition of the mixture. The resulting powders were sintered at 1000 °C for 2 h in air.

Due to the increased evaporation of lithium with smaller particles sizes, the sol-gel synthesis wasn’t suitable for Li₅AlO₄ as only LiAlO₂ resulted. A bulk powder approach was used instead, with mixing 3.75 g (10 mmol) aluminium nitrate nona hydrate with 1.31 g (55 mmol, 10mol% excess) lithium hydroxide. The mixture was sintered at 750 °C for 24 h in argon atmosphere.

Results and discussion

Lithium aluminum oxides

With phase equilibrium thermodynamics, the eutectic composition of the Li₂O-Al₂O₃ system is determined. By applying CALPHAD²⁷(Calculation of Phase Diagram) with a database described in²⁸,³⁰,³³ the eutectic composition is identified to be 0.22. Additionally, the CALPHAD modelling predicts the compounds LiAlO₂ and Li₅AlO₄ which are formed during solidification at this certain composition. Based on this information, the synthesis procedure was set up in this work, summarized in Table 3. The compositions of Al:Li of 0.17, 0.50, and 0.83 yield the stoichiometric compounds Li₅AlO₄, LiAlO₂, and LiAl₅O₈ which are selected for this study. The predicted high temperature aluminate LiAl₁₁O₁₇ which is found at high aluminum concentrations has no common stability zone with the EnAM LiAlO₂ and was therefore not considered in the models at this point. The compounds were synthesized via the sol-gel route as described in the experimental section. The targeted composition was evaluated by inductively coupled plasma optical emission spectrometry (ICP-OES). The elemental balance of target and final compound are displayed in Table 3.

The elemental determination confirms the expected stoichiometries for all three compounds. The structure of the compounds was validated by powder X-ray diffraction. The diffractograms exhibit a low background and in general only the expected reflexes. The stoi-
Table 3: Fraction of lithium oxide and aluminium oxide in the stoichiometric compounds; theoretical and synthesis

<table>
<thead>
<tr>
<th>Compound</th>
<th>Target Li$_2$O:Al$_2$O$_3$</th>
<th>Product Li$_2$O:Al$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_5$AlO$_4$</td>
<td>0.833:0.167</td>
<td>0.829:0.171</td>
</tr>
<tr>
<td>LiAlO$_2$</td>
<td>0.500:0.500</td>
<td>0.496:0.504</td>
</tr>
<tr>
<td>LiAl$_5$O$_8$</td>
<td>0.167:0.833</td>
<td>0.158:0.842</td>
</tr>
</tbody>
</table>

Chiometry as well as the diffractogram confirm the synthesis of Li$_5$AlO$_8$, LiAlO$_2$, and Li$_5$AlO$_4$ (figure 3). The viscosity of Li$_5$AlO$_4$ was studied for comparison with the MD results.

![Diffractograms of LiAl$_5$O$_8$, LiAlO$_2$ and Li$_5$AlO$_4$ with references from PDF2 database](image)

**Figure 3:** Diffractograms of LiAl$_5$O$_8$, LiAlO$_2$ and Li$_5$AlO$_4$ with references from PDF2 database$^{37-39}$

Viscosity and ion diffusivity are decisive information for gaining a better understanding on the solidification of melts. The diffusivity and viscosity were calculated from MD simulations of Li$_5$AlO$_4$, LiAlO$_2$, and LiAl$_5$O$_8$ at temperature spanning from solid state to the phase transition and the molten state. Experimentally, the viscosity and melting point of the relatively low melting compound Li$_5$AlO$_4$ was accessible using melt-microscopy.$^{35}$ The
individual ion diffusivity were exclusively available from the MD simulations. In the follow-
ing we will describe the results obtained from MD simulations, i.e. diffusivity of the ions and viscosity of the compounds at high temperatures.

**Individual ion diffusivity**

The MD simulations allow studying the position of the individual ions \( \text{Li}^+ \), \( \text{Al}^{3+} \) and \( \text{O}^{2-} \) over time. The simulations were performed for all three compounds and at the end of this subsection ion diffusivity in all three compounds are compared. However, for a concise presentation we illustrate the results for LiAlO\(_2\), which has been already identified as potential EnAM. The corresponding illustration for the other compounds are shown in the supplementary information. The higher the temperature, the more random the positions of the ions are. This can be illustrated by snapshots of the simulated cube and the radial distribution functions (RDF). In figure 4 this is illustrated for LiAlO\(_2\) at 300 K, 1700 K which is close to the liquidus temperature, and 2000K which is above the liquidus temperature. The snapshots visualize the degree of disorder increasing with temperature. The RDF at 300 K exhibits the inter-ionic distances as expected in a LiAlO\(_2\) crystal (space group P4\(_1\)2\(_1\)2). The distances of the individual ion pairs are described by quite narrow distributions (see coloured lines in figure 4). At 1700 K the distributions have significantly broadened, at 2000 K the RDF displays the characteristics of a liquid.

It is visible in the RDF that some distance distributions broaden more than others with increase in temperature. For example, the Al-O distance distribution remains relatively narrow, whereas distances between \( \text{Li}^+ \) and other ions become more random. This is also seen in the RDFs the other two compounds (figure S1 and S4). The mobility of the ions is described by their mean square displacement (MSD). It can be computed for each individual ion and then averaged over all ions of the species, and it is a measure of their diffusivity. The diffusion coefficient \( D \) is calculated from the mean-square displacement of the lithium, aluminium, and oxygen ions according to equation 2.
Figure 4: Structural snapshots and radial distribution function (RDF) of LiAlO$_2$ at (a) the initial state at T = 300 K, (b) T = 1700 K, and (c) T = 2000 K.

$$D(t) = \frac{1}{6\delta t N_{\text{ion}}} \sum_{i=1}^{N_{\text{ion}}} \left[ |\mathbf{r}_{(i)}(t) - \mathbf{r}_{(i)}(0)|^2 \right]$$

In the equation $t$ denotes the time and the above sum is carried out over the number of ions $N_{\text{ion}}$.

The MSD of all three lithium aluminum oxides at 2500 K clearly shows that Li$^+$ is the most mobile of the ions, which is shown here for LiAlO$_2$ (figure 5, for the others see S2 and S5). This is well in agreement with the literature, where the lithium-ion activation energy was found being lower compared to other ions, i.e. 0.53 eV. Our approach allows us to determine diffusivity of all three ions during phase transition of the Li-Al-Oxides, shown here for LiAlO$_2$ (figure 6, for the others see S3 and S6) where a rapid increase of all ions’ diffusion between 1800 K and 1900 K is observed. Some results of the LiAlO$_2$ are shown in Table 4.

These results match quite well with the simulations of Jacobs et al. They studied lithium diffusion in LiAlO$_2$ with respect to its application in nuclear fusion. Here, however,
Figure 5: Mean-square displacement of Li⁺, Al³⁺ and O²⁻ in LiAlO₂ at T = 2500 K

Table 4: Diffusion coefficients $D \ (10^{-9} \text{ m}^2 \text{ s}^{-1})$ of the constituting ions of LiAlO₂ at different temperatures at the phase transition and lithium diffusion coefficients from the literature

<table>
<thead>
<tr>
<th>Ions in LiAlO₂</th>
<th>T = 1700 K</th>
<th>T = 1800 K</th>
<th>T = 1900 K</th>
<th>T = 2000 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>3.0</td>
<td>5.0</td>
<td>9.6</td>
<td>10.5</td>
</tr>
<tr>
<td>Li (Jacobs et al.) [40]</td>
<td>8.9</td>
<td>10.9</td>
<td>13.0</td>
<td>15.2</td>
</tr>
<tr>
<td>Al</td>
<td>0</td>
<td>0</td>
<td>0.9</td>
<td>1.2</td>
</tr>
<tr>
<td>O</td>
<td>0</td>
<td>0</td>
<td>1.5</td>
<td>1.9</td>
</tr>
</tbody>
</table>

we examine besides LiAlO₂ the higher and lower lithiated compounds Li₅AlO₄ and LiAl₅O₈ which according to the thermodynamic model can form in lithium-ion battery recycling slags depending on the actual composition. From the MD simulation of all compounds, it is evident that the lithium ions are more mobile in the lithium-rich compounds Li₅AlO₄ and LiAlO₂ (figure 7). Its diffusion coefficient at T = 2500 K in the lithium-poor LiAl₅O₈ is only approx. one third ($D = 12 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) of the one in the lithium-rich Li₅AlO₄ ($D = 32 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$). The mobility of aluminium ions and oxygen ions seems to decrease with decreasing lithium content, however this is not significant.
Figure 6: Diffusion coefficient of Li\textsuperscript{+}, Al\textsuperscript{3+} and O\textsuperscript{2−} in LiAlO\textsubscript{2} at temperatures from 1500 K to 2700 K

Losses of lithium to the gas phase have been observed during the optimization of their Li-Al-Oxide compound synthesis. An enrichment of \textit{approx.} 70\% of lithium in the flue dust is described in the literature in a small scale lithium-ion battery pyrometallurgical recycling approach.\textsuperscript{41} Its relatively high diffusivity may contribute to its tendency to transfer from the molten to the gas phase.

**Viscosity depending on Li:Al ratio**

The viscosity of the Li-Al-oxide discussed here is accessible from the diffusion coefficients obtained from the MD simulation (equation 2) using equation 3.

$$\eta = \frac{kT}{3\pi\lambda D}$$  \hspace{1cm} (3)

In equation 3, $\eta$ is the viscosity, $k$ the Boltzmann constant, $T$ the absolute temperature,
Figure 7: Composition dependence of the self-diffusion coefficient of Li$^+$, Al$^{3+}$ and O$^{2-}$ at $T = 2500$ K

$D_s$ the diffusion coefficient, and $\lambda$ is the translation distance of the diffusing ion which is always considered to be 2.8 Å, the diameter of oxygen.$^{42-44}$ The temperature dependence of the viscosity of the three Li-Al-oxides is shown in figure 8. A strong decrease of the viscosity is observed above the liquidus temperature, which is lowest for the Li$_5$AlO$_4$ and highest for the LiAl$_5$O$_8$ composition. It appears that the higher the lithium content of the melt, the lower the viscosity, which indicates that a high content of lithium promotes phase separations in the liquidus and with that can govern the formation of the solid compounds. Experimentally, the viscosity is available with high confidence for the low melting Li$_5$AlO$_4$. It was determined to be 2.5 mPa s at 1328 K matching well the simulated viscosity at this temperature of 2.2 mPa s. The two other compounds did not show melting up to 1500 K accessible with the microscope. The observable high temperature behaviour of the compound is in accordance with the CALPHAD and MD model.

The knowledge of the melt viscosity is highly valuable as it influences the kinetics of
solidification and can contribute to phase separations. Liquidus separation into immiscible phases can be predicted based on thermodynamics, taking the enthalpy and the entropy of mixing into account. If the enthalpy of mixing is positive, it exists a critical temperature below which phase separation is spontaneous. Kinetic parameters, especially the viscosity, are decisive for the phase separation actually to occur. Low viscosity will quickly yield a phase separation, whereas viscous melts will separate very slowly. Phase separation in molten slags has not been described very detailed on a molecular level in the literature. Liquid-liquid immiscibility, is more extensively studied as a common phenomenon in glass forming melts.\textsuperscript{13,14} Actually, far more binary glass forming melts exhibit liquid-liquid immiscibility than exhibit homogeneous liquid behaviour.\textsuperscript{45} Though, thermodynamics predict
phase separation for many glasses, due to high viscosity those are not always observed.\textsuperscript{11,12} Once separated, the phases exhibit different compositions, melting points, ion mobility and viscosity. With respect to tailor EnAMs in slag systems, knowledge of ion mobility and viscosity of the potential compounds will be a key parameter, and it can be obtained by MD simulations as shown here.

**Individual ion coordination number depending on composition**

The experimental results agree with the findings of the simulations, which increases the confidence in the other simulated parameters at high temperatures. These are difficult to assess experimentally. The simulation can potentially yield further information on melt structure. The mean coordination numbers are determined by extracting the positions $r$ corresponding to the initial peaks in their respective radial distribution functions (figure 4). One interesting observation is the increase in the mean coordination number of Li$^+$ and Al$^{3+}$ in the melt, comparing the three compounds from high to low lithium contents. The mean coordination number of Li$^+$ in Li$_5$AlO$_4$ is \textit{approx.} 3 and increases to 4 in the LiAl$_5$O$_8$. The mean coordination number of Al$^{3+}$ in Li$_5$AlO$_4$ is \textit{approx.} 4 and increases to 5 in the LiAl$_5$O$_8$. The coordination number in the melt can steer the structure of the solidified compound. Of course, the simulations have limitations, \textit{e.g.}, they do not account for elemental transitions to gas phase. During the simulation, the number of elements is always conserved.

**Conclusions**

In this work we study melt characteristics of the three stoichiometric compounds in the Li$_2$O-Al$_2$O$_3$ system, \textit{i.e.} Li$_5$AlO$_4$, LiAlO$_2$, and LiAl$_5$O$_8$. Our rational is, that when we learn about viscosity of certain compositions and diffusivity of the constituent ions, conclusion helping the prediction of phase separation and solidification can be derived. We have chosen the Li-Al-O system because LiAlO$_2$ has been identified previously as a promising phase to recover
lithium from lithium-ion battery recycling slags. Initially, the eutectic composition in terms of LiAlO\(_2\) and Li\(_5\)AlO\(_4\) is calculated under CALPHAD framework. We have then simulated the molecular dynamics of the three stoichiometric compounds at temperatures from below to well above the liquidus temperature and determined the viscosity of each compound with increasing temperature. Additionally, we determined the diffusivity of Li\(^{+}\), Al\(^{3+}\), and O\(^{2-}\) for each compound and each temperature. The viscosity was well in agreement with those obtained from literature and from reference compounds synthesized by the sol-gel route. It can be concluded that Li\(^{+}\) already diffuses at temperatures below the liquidus. Its diffusion coefficient is about ten times higher than that of Al\(^{3+}\) at the melting point in, i.e. LiAlO\(_2\). This implies that the availability of Li\(^{+}\) is not a limiting factor in the crystal formation of Li-Al-O rich melts. The results of the MD simulation and the experiments show that the viscosity increases with decreasing lithium content. This finding suggests that lithium rich melts are more fluid and high lithium concentrations will promote liquidus phase separation, and it could be an interesting topic for thermodynamics in the future. In conclusion, we have gained in valuable insight into the melt characteristics of the Li-Al-oxides, which will be important for understanding compound formation in slags with respect to recycling critical elements.

**Author Contributions**

Sven Hampel: Investigation, Writing – Original Draft, Visualization, Iyad A. Alhafez: Investigation, Visualization, Writing – Original Draft, Thomas Schirmer: Supervision, Writing – Review and Editing, Funding Acquisition, Nina Merkert: Supervision, Writing – Review and Editing, Funding Acquisition, Alena Schnickmann: Investigation, Haojie Li: Investigation, Michael Fischlschweiger: Supervision, Writing – Review and Editing, Funding Acquisition, Ursula E.A. Fittschen: conceptualization, supervision, Writing – Review and Editing, Funding Acquisition.
Conflicts of interest

There are no conflicts to declare.

Acknowledgement

The authors thank the Deutsche Forschungsgemeinschaft (DFG) for funding of this work within the Priority Program "Engineered Artificial Minerals (EnAM) – a geo-metallurgical tool to recycle critical elements from waste streams (SPP 2315)", project numbers 470367641, 470309740, and 470323858.

Supporting Information Available

The following files are available free of charge.

- supporting information: modelling results for the compounds Li5AlO4 and LiAl5O8

References


(4) Olivetti, E. A.; Ceder, G.; Gaustad, G. G.; Fu, X. Lithium-Ion Battery Supply Chain


(29) Li, H.; Ranneberg, M.; Fischlschweiger, M. High-Temperature Phase Behavior of Li2O-MnO with a Focus on the Liquid-to-Solid Transition. *JOM* **2023**,


