

Article

Molten Salt Electrolyte for Na-ZnCl₂ All-Liquid Battery for Grid Storage

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Abstract: Zeolite Battery Research Africa (ZEBRA) batteries (Na-NiCl₂ solid electrolyte batteries, SEBs) have commercial applications in energy storage due to their low costs and recyclability, long lifetime, and high safety. In commercial ZEBRA batteries, Ni electrode and beta-alumina solid electrolyte (BASE) have a more than 70% share of the overall cell material costs. Na-ZnCl₂ all-liquid batteries (ALBs), which replace Ni with abundant and low-cost Zn and BASE electrolyte with molten salt electrolyte, could reduce costs and provide a longer lifetime and higher safety, making their application in grid storage promising. However, compared to SEBs, ALBs are in an early development stage, particularly for their molten salt electrolytes, which have a significant effect on the battery performance. Physical and chemical properties of the salt electrolyte like melting temperatures and solubilities of electrode materials (i.e., Na and Zn metal) are vital for the molten salt electrolyte selection and battery cell design and optimization. In this work, the binary and ternary phase diagrams of salt mixtures containing NaCl, CaCl₂, BaCl₂, SrCl₂, and KCl, obtained via FactSage simulation and DSC measurements, as well as the solubilities of electrode materials (Na and Zn metals), are presented and used for the selection of the molten salt electrolyte. Moreover, various criteria, considered for the selection of the molten salt electrolyte, include high electromotive force (EMF) for suitable electrochemical properties, low melting temperature for large charge/discharge range, low solubilities of electrode materials for low self-discharge, low material costs, and high material abundance for easy scale-up. Based on these criteria, the NaCl-CaCl₂-BaCl₂ and NaCl-SrCl₂-KCl salt mixtures are selected as the two most promising ALB molten salt electrolytes and suggested to be tested in the ALB demonstrators currently under development.

Keywords: differential scanning calorimetry (DSC); FactSageTM thermodynamic simulation; phase diagram; solubilities of electrodes; Zeolite Battery Research Africa (ZEBRA) battery



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1. Introduction

As an alternative to commercial sodium sulfur batteries, ZEBRA batteries (Na-NiCl₂ solid electrolyte batteries, SEBs) have commercial applications since the starting of this century in energy storage, energy back up, transportation, etc. [1–3], due to their low costs, easy recyclability, long lifetime, and high safety [4]. In the commercial ZEBRA batteries, Ni electrode and beta-alumina solid electrolyte (BASE) have a larger than 70% share of

the overall cell material costs [5]. By using abundant and low-cost Zn as an alternative to Ni, the next-generation ZEBRA battery (called here next-gen ZEBRA), i.e., Na-ZnCl₂ SEB, could have much lower cell material costs [6]. Na-ZnCl₂ all-liquid batteries (ALBs) replace (in addition to Zn replacement) the BASE electrolyte of the Na-ZnCl₂ SEB with a molten salt electrolyte for even lower costs, easier recyclability, longer lifetime, and higher safety [7]. Compared to the commercial ZEBRA cells (operating at ~300 °C), the Na-ZnCl₂ ALB cells do not use a BASE primary electrolyte, which reduces the cell costs and makes the scale-up easier [7,8]. It has a higher operating temperature (~600 °C) to be able to function in an all-liquid state, which improves performance. This boosts the ability to dis-/charge at high current density [7,8].

In the commercial ZEBRA battery with a BASE primary electrolyte, AlCl₃-NaCl-NiCl₂ is used as a molten salt electrolyte, which consists of a secondary electrolyte (NaAlCl₄) with the melting temperature of ~150 °C and partly active electrode components (NaCl and NiCl₂) [5]. Leonardi et al. (2023) reviewed the most recent research and development on materials and cell design of all sodium–metal chloride batteries (Na-NiCl₂, FeCl₂, CuCl₂, ZnCl₂, etc.) with a wide perspective [9]. In this review, alternative formulations to conventional nickel cathodes and advanced ceramic electrolytes were discussed in particular, referring to the current research challenges on cost reduction, lowering of the operating temperature, and performance improvements [9]. Moreover, a comprehensive overview of the commercial tubular cell design and prototypal planar design was presented, highlighting advantages and limitations based on the analysis of research papers, patents, and technical documents [9]. Recently, to improve rate capability and life cycle of the commercial ZEBRA battery, Xiong et al. (2024) worked on a rational structure design of metal-based cathode via mixing NiFe nanowires with NaCl as the composite cathode or designing a graphene anchoring porous nickel nanostructures as a cathode [10,11].

The difference between the next-gen ZEBRA and the commercial ZEBRA battery is that by replacing Ni with Zn, it has the electrochemical reaction of $\text{ZnCl}_2 + \text{Na} \leftrightarrow 2\text{NaCl} + \text{Zn}$ (~2 V at ~300 °C) during charging/discharging [6]. In the work of other research groups and our previous work, the adapted ZEBRA battery (next-gen ZEBRA mentioned above) has been intensively studied for its electrolyte and cell design [6,12–14], dis-/charge reaction mechanisms [12,15], cell upscaling [16], etc., based on the previous research, mainly on the commercial ZEBRA batteries [9–11]. Sieuw et al. (2024) investigated the influence of precursor morphology and Zn cathode processing on the performance and life cycle of the next-gen ZEBRA cell at 300 °C [12]. Moreover, the dis-/charge cycling performance of Na-ZnCl₂ cells was correlated with the ternary ZnCl₂-NaCl-AlCl₃ phase diagram, and mass transport through the secondary NaAlCl₄ electrolyte was identified as an important contribution to the cell resistance [12]. These insights enable the optimization of the design of the battery cell, e.g., having tailored cathode microstructures. Kumar et al. (2023) studied the AlCl₃-NaCl-ZnCl₂ salt electrolyte of the next-gen ZEBRA (Na-ZnCl₂) battery in depth [13]. Experimental and modeling methods were used to examine its binary and ternary phase diagrams and vapor pressures theoretically via FactSage simulation and experimentally via differential scanning calorimetry (DSC) and a melting point apparatus (OptiMelt™) [13]. These findings have been successfully correlated with the cell performance and could be used in future cell improvements [12].

This simulation-assisted method, based on thermodynamic simulation via FactSage™ and thermal analysis via DSC and OptiMelt™, has also been successfully applied for the selection of a molten salt electrolyte for liquid metal batteries (LMBs), which are another group of batteries using liquid metals and molten salts [17,18]. A low-melting-point NaCl-LiCl-KCl molten salt electrolyte was selected for a Na-based LMB (Na-LMB) based on the phase diagram and other experimental data [17]. The Na-LMB test cell with the

selected molten salt electrolyte shows an energy efficiency of about 80% and a Coulombic efficiency higher than 97% [18]. Moreover, the levelized cost of storage (LCOS) of the Na-LMB system with the selected NaCl-LiCl-KCl molten salt electrolyte was estimated to be 0.027–0.029 USD/kWh for scaled application conditions, based on a 1MW/5 MWh demonstrator energy storage plant made of 100 Ah cells [18].

As opposed to the ZEBRA battery, AlCl_3 salt cannot be used in the molten salt electrolyte of Na- ZnCl_2 ALB since it does not use a solid ceramic electrolyte to separate the Na electrode and molten salt electrolyte; thus, AlCl_3 can spontaneously react with the contacted Na metal anode (see Figure 1(right)). To avoid spontaneous reactions of the salt with Na, which lead to co-reduction and safety issues, the chloride salts, namely, CaCl_2 , BaCl_2 , KCl , SrCl_2 , LiCl , whose electromotive forces (EMFs) are higher than Na/NaCl [19] should be preferred. The safety concern caused by the high vapor pressure ($>>10$ atm) of AlCl_3 at the operating temperature of 600 °C of the ALB provides an additional disadvantage to its use [13]. The above-mentioned chloride salts have low vapor pressures and will, therefore, be a preferred choice for the molten salt electrolyte for Na- ZnCl_2 ALB. Moreover, to have a large dis-/charge range of the cell, the molten salt electrolyte needs to have a low melting temperature since the formed NaCl during discharging rapidly increases the melting temperature of the salt mixture electrolyte.

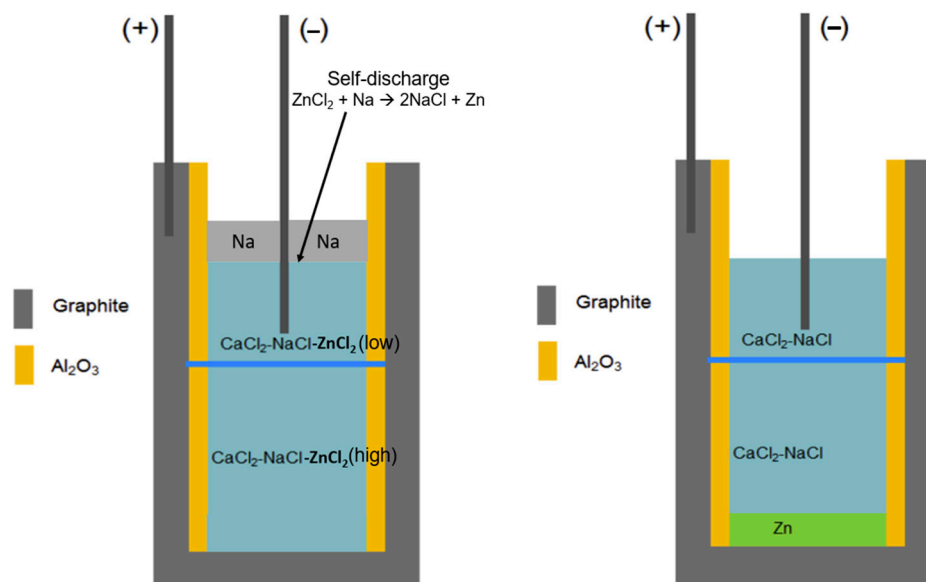


Figure 1. A schematic of a Na- ZnCl_2 ALB cell with a NaCl- CaCl_2 molten salt electrolyte in a fully charged state (left) [7] and a fully discharged state (right) with a porous ceramic diaphragm (blue line). It has the electrochemical reaction of $\text{ZnCl}_2 + \text{Na}$ (charged) $\leftrightarrow$ $2\text{NaCl} + \text{Zn}$ (discharged) during charging/discharging.

Xu et al. (2016) [7] and Xu et al. (2017) [8] used a eutectic NaCl- CaCl_2 (50:50 mol%) electrolyte in their ALB cells (see Figure 1). CaCl_2 has the EMF of 3.462 V, higher than but close to that of NaCl (3.424 V) [19]. The co-reduction of Ca in Na electrode was observed during charging [7]. This could lead to the formation of Ca-Na-Zn intermetallic compounds responsible for the multiple discharge plateaus of the ALB cell [20]. Moreover, it could lead to lower CaCl_2 content in the molten salt electrolyte compared to the ideal charging (without co-reduction). The molten salt electrolyte with lower CaCl_2 content than the eutectic mixture has an increased melting temperature, as shown in the NaCl- CaCl_2 phase diagram [21]. The NaCl- CaCl_2 (50:50 mol%) electrolyte used in the ALB cell of Xu et al. (2016) [7] has a eutectic melting temperature of about 500 °C [7,21]. The increased melting temperature could have significant negative effects on the battery performance, e.g., a

reduced charge/discharge range. The cell testing shows that the discharge flat voltage of the ALB cell at 560 °C is in the range of about 1.4 V to 1.8 V, and the cycle coulombic efficiency achieved is about 90% at low discharge current densities (below 40 mA/cm²) [7]. In the ALB cell, as shown in Figure 1, a porous ceramic diaphragm (blue line in Figure 1) is used to separate the molten salt electrolyte into two compartments and, thus, slow the Zn²⁺ transport down from bottom to top in order to reduce the self-discharge rate. The self-discharge of this ALB is mainly caused by a reaction of Zn²⁺ with Na metal [7,8]. Thus, the solubility of Na metal in the molten salt electrolyte has a significant effect on self-discharge, although, using the diaphragm, the self-discharge rate is still high. The open circuit voltage is about 1.83 V in the fully charged state. After leaving the cell at open circuit for 9 h, the open circuit voltage value drops to 1.69 V, while it decreases to 1.6 V after 10 h [7]. This means the charged cell is almost fully discharged after 10 h due to self-discharge.

To improve the cell design and fabrication of the Na-ZnCl₂ ALB, recently, some techniques like neutron imaging [22] and cell modeling [23] were developed and used. Sarma et al. (2024) [22] used in situ dynamic neutron radiography to develop a reusable, hermetically sealed, high-temperature, and sufficient corrosion-resistant cell in order to enable long-term cycling of the Na-Zn battery in a realistic environment. The design, as well as various approaches for assembling and filling the cell, was also presented in their study [22]. Godinez-Brizuela et al. (2023) [23] developed a continuous multiphase model for liquid metal—molten salt batteries, including LMBs and the ALB batteries—studies in their work. It used the Na-ZnCl₂ ALB with the NaCl-CaCl₂ electrolyte as the model system. The simulation model can simulate the changes in electrode and electrolyte volume during charging and discharging, and resolve the spatial variations in the chemistry of the electrolyte that accompany the interfacial reactions. It was found that volume change and species redistribution were important in predicting the maximum theoretical capacity of the cell when neglecting other transport mechanisms. Weber et al. (2024) performed a risk assessment for the Na-ZnCl₂ ALB according to ISO 12100 [24] to minimize the risks involved in the battery fabrication and operation [25]. Hazard identification and risk evaluation were systematically addressed, including a thorough literature review, theoretical calculations, and selected experiments. Cell overpressure was found to be one of the main risks. Overpressure might be caused either by mistakes in battery production (humidity) or operation (overcharge/discharge). In terms of cell housing, the feedthrough was identified as the weakest component. Its failure might lead to the release of hazardous aerosols into the environment. In this context, the candidate electrolyte components LiCl and BaCl₂ were identified as dangerous salt components [25].

Overall, the molten salt electrolyte is a key part of the ALB and could significantly affect its storage performance, operation safety, economics, and environmental impact. For its selection, key factors such as melting temperature, material cost, EMF, electrode solubility, salt vapor pressure, and environmental impact needed to be considered. Besides some references on ALB with a NaCl-CaCl₂ molten salt electrolyte mentioned above, to the best of our knowledge, an in-depth study on the molten salt electrolyte for ALB has not been conducted, and there is no available literature showing the methods and results for such molten salt ALB electrolyte selection. This work focuses on the molten salt electrolyte selection for ALB by considering these key factors.

In this work, the promising molten salt electrolytes for the Na-ZnCl₂ ALB cell containing NaCl, CaCl₂, BaCl₂, SrCl₂, and/or KCl are selected based on the data such as phase diagrams of salt mixtures (Section 3.1, screening), EMFs of single salts, and material costs (Section 3.2, pre-selection), which are available in the literature or obtained from simulation and experiments in this work. Since LiCl has a high material cost [26] and the ALB uses a

large amount of the salt electrolyte, LiCl is not considered for the molten salt electrolyte here. In this work, the promising molten salt electrolytes mentioned above were investigated in-depth with thermodynamic simulation via FactSageTM (Section 3.1) and thermal analysis via DSC (Section 3.3). Moreover, the solubilities of Na and Zn electrodes in the selected promising molten salt electrolytes were measured with an analysis method based on salt titrations (Section 3.4). Overall, this paper presents these simulated and measured data of the key thermal properties of salt systems for Na-ZnCl₂ ALBs. These properties can also be used for the battery design, optimization, and operation. The presented simulation and experimental methods for molten salt electrolyte selection used in this work could also be implemented with other salt-based electrolyte batteries.

2. Materials and Methods

This section describes the methods used to select the promising molten salt electrolytes in ALB based on their various characteristics, such as phase diagrams for battery improvement. Chloride salt mixtures are promising molten salt electrolytes for molten salt batteries due to their high thermal and electrochemical stabilities and low costs [7,17,27]. As shown in Figure 1(left), NaCl in the molten salt electrolyte acts as a source of Na, forming a negative electrode during charging. However, NaCl has a melting temperature higher than 800 °C [26]. By adding other chloride salts, the melting temperature can be significantly reduced due to the eutectic effect, for example, eutectic NaCl-MgCl₂-KCl has a melting temperature of <400 °C [26]. Thus, in this work, NaCl was investigated in combination with other chloride salts with low costs and high EMFs (i.e., CaCl₂, BaCl₂, SrCl₂, and KCl) in binary and ternary systems in order to select promising molten salt electrolytes based on the key factors like melting temperature, electrode solubilities (self-discharge), material costs, and EMFs (co-reduction issue of the Na electrode). In this work, it is assumed in the selection of molten salt electrolytes that the porous ceramic diaphragm in the ideal ALB cell (see Figure 2) can perfectly prevent the diffusion of Zn²⁺ from bottom to top, i.e., prevent the main self-discharge reaction at the interface of Na electrode with Zn²⁺ in the salt, as shown in Figure 1(left). Moreover, in charge/discharge of the ALB cell, the molten salt electrolyte above the diaphragm has a higher melting temperature than that below the diaphragm, due to a higher content of NaCl and a lower content of ZnCl₂. **Thus, for simplicity, the molten salt electrolyte selection in this work is based on the molten salt electrolyte above the diaphragm of the ideal ALB cell, which does not contain ZnCl₂.**

In this work, firstly, the simulations via FactSage (Version 8.1) were performed to obtain information like melting temperature (phase diagrams) and melting behavior for the selection of the promising molten salt electrolytes. Secondly, the selected salt mixtures were prepared in a moisture-free inert environment inside a glovebox and used in DSC experiments to evaluate the FactSage simulation results. After that, the experiments of the solubilities of the electrode materials (i.e., Na and Zn) in the selected salt mixtures were performed in an oven inside the glovebox. The metal solubilities were measured with a titration method previously developed by our DLR group [17].

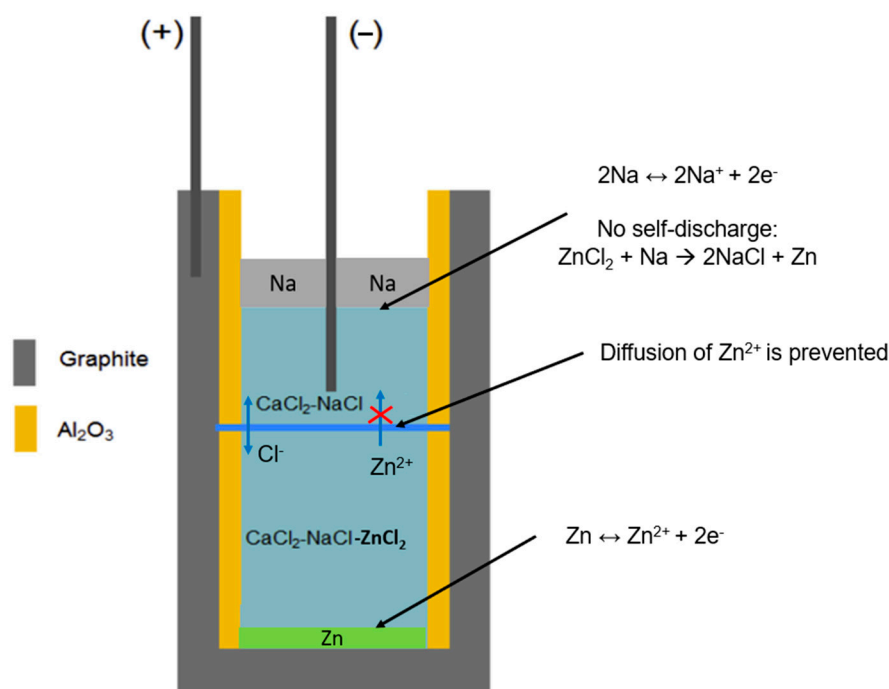


Figure 2. A schematic of an ideal Na-ZnCl₂ ALB cell with a NaCl-CaCl₂ molten salt electrolyte and an ideal porous ceramic diaphragm (blue line), which can completely prevent the diffusion of Zn²⁺ from bottom to top (i.e., self-discharge).

2.1. FactSageTM Thermodynamic Simulation

FactSage is a commercial thermochemical database system with modules of information, database, calculation, and manipulation [28]. The calculation modules of FactSage contain the main function modules of FactSage, including Reaction, Predom, EpH, Equilib, Phase Diagram, and Optisage. These calculation modules are based on the minimum Gibbs free energy (G) and CalPhaD (Calculation of Phase Diagrams) methodology. For a system (e.g., a salt mixture in this work) at a constant temperature (T) and pressure (P), the equilibrium state is the one with the lowest possible Gibbs free energy G . Mathematically, G is expressed as:

$$G = H - TS \quad (1)$$

where H is the enthalpy and S is the entropy of the system. FactSage's calculation modules work to find the composition of phases that results in the absolute minimum G for the given conditions (temperature, pressure, and overall composition). To calculate the minimum, a comprehensive methodology called CalPhaD is used [29]:

1. The CalPhaD methodology was introduced in the 1960s by Larry Kaufman. The essence is the optimization of the Gibbs energy functions to reproduce the known phase diagrams and utilize it to make the prediction of unknown phase equilibria.
2. CalPhaD relies on extensive databases containing thermodynamic properties (like Gibbs energy functions). FactSage gives access to databases of thermodynamic data for thousands of compounds, as well as to evaluated and optimized databases for hundreds of liquid and solid metals, liquid and solid oxides, molten and solid salts, and aqueous solutions [28]. These databases are built through a combination of experimental data (e.g., calorimetry, phase equilibrium measurements) and theoretical modeling.
3. For solution phases (e.g., molten salt phases in this work), CalPhaD employs thermodynamic models to describe how the Gibbs energy of the phase changes with composition. Common models include: Ideal Solution Model, Regular Solution Model, Subregular Solution Model, Compound Energy Formalism (CEF), etc.

4. To find the minimum Gibbs energy, FactSage employs sophisticated numerical optimization algorithms. These algorithms iteratively adjust the amounts and compositions of different phases until the system reaches its lowest G. Common methods include Newton–Raphson methods, linear programming techniques, etc.

This work utilizes Version 8.1 of FactSage. The Phase Diagram module and the database FTSalt were used to obtain the phase diagrams of selected binary/ternary salts of NaCl, CaCl₂, BaCl₂, SrCl₂, and KCl. Moreover, the Equilib module was selected to plot Δc_p (J/K/mol) vs. T (°C). The plots were compared with the DSC experiments performed to confirm the melting temperature and melting behavior.

2.2. Sample Preparation for DSC and Solubility Analysis

For differential scanning calorimetry (DSC), anhydrous salts with a purity of >99% (NaCl, 99%, Merck KGaA, Darmstadt, Germany/Thermo Scientific Chemicals, Dreieich, Germany; KCl 100%, VWR International, Darmstadt, Germany; SrCl₂, ultra dry, 99.995%, Thermo Scientific Chemicals, Germany; CaCl₂, 99%, Merck KGaA, Darmstadt, Germany; BaCl₂, 99%, Merck KGaA, Germany) were used to prepare the salt mixtures. Due to strong hygroscopicity of chloride salts (particularly CaCl₂, BaCl₂, SrCl₂), the storage, weighing, mixing, and sample preparation of the salts were carried out in a glovebox (GS Glovebox Systemtechnik GmbH, Malsch, Germany, Glovebox Mega 2, O₂ < 0.5 ppm, H₂O < 1 ppm) swept with ultra-high-purity argon gas (Ar 5.0, purity > 99.999%). All salt mixtures (~1 g) for thermal analysis were ground in a ceramic mortar for at least 30 min by hand so that they were well mixed with an acceptable small salt particle size for thermal analysis with DSC.

For solubility analysis of Na and Zn electrode metals in the molten salts, anhydrous salts with a purity of >99% (NaCl, 99%, Merck KGaA, Germany/Thermo Scientific Chemicals, Germany; KCl 100%, VWR International, Germany; SrCl₂, 99%, Fischer Scientific, Germany; CaCl₂, 99%, Merck KGaA, Germany; BaCl₂, 99%, Merck KGaA, Germany) were used to prepare the salt mixtures. Same as the salt mixture samples for DSC, their storage, weighing, mixing, and sample preparation were carried out in the glovebox swept with ultra-high-purity argon gas. Moreover, the Na and Zn metals with a purity of >99% (Thermo Scientific Chemicals, Germany) were used in the measurements.

2.3. Differential Scanning Calorimetry (DSC) for Thermal Analysis

DSC is a powerful thermo-analytical technique to measure the melting temperature and phase change enthalpy of the tested sample, such as a salt [30]. Normally, in a DSC measurement, the temperature of the sample is increased linearly and compared to an empty reference crucible (see Figure 3b). A sample of known mass (e.g., about 20 mg salt mixture in this work) is placed in a sample crucible and then heated/cooled at a constant rate (e.g., 10 K/min) under sweeping of Ar 5.0 at 100 mL/min. The behavior of the heat flow inside the sample can reveal the thermal information about the melt, for example, glass transitions, phase changes, curing, and melting. This method has been successfully used by many research groups, including our group, to measure, e.g., the melting temperatures of the salt mixtures for thermal energy storage [31] or of salt electrolytes in molten salt batteries, like liquid metal batteries [17,18] and metal–chloride batteries [13].

A high-temperature DSC 404[®] (Netzsch, Selb, Germany) oven (see Figure 3a) was used to study the melting process of the selected salts. The holder inside the oven with two slots for the placement of crucibles is shown in Figure 3b. In this work, gold-plated stainless steel (SS) and Ni-based 2.4816 alloy crucibles from Netzsch, Germany, were used in a closed state with a maximum operation temperature of about 600 °C (gold-plated stainless steel) and 650 °C (Ni-based). Such high temperatures are required for this work since the salt electrolyte should be liquid at the ALB working temperature of around 600 °C.

Before testing the desired samples by DSC, a temperature calibration was carried out to ensure accurate readings of the instrument. Standard reference materials with known melting points were used to perform temperature calibration. Additionally, several baseline measurements were carried out before each sample measurement to ensure that the DSC instrument records a stable and accurate baseline. This involves running an empty pan with a reference pan so that it records a flat or near-zero heat flow signal. Inside the glovebox, a tool kit was used to seal the crucibles tightly (with or without salt sample). Subsequently, the crucibles were washed to rinse off any salt contaminants from the outer surface and dried before being placed in the DSC device. In every DSC measurement, 3–4 cycles were repeated for every salt sample in this work to get reliable results.

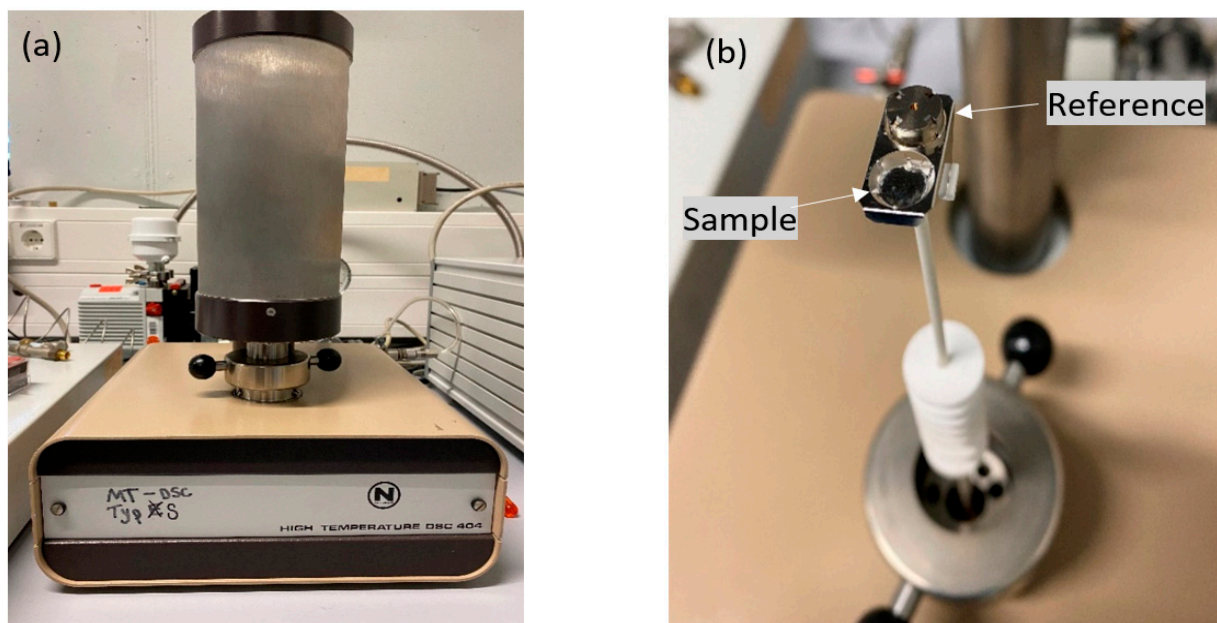


Figure 3. (a) Netzsch DSC 404[®] for DSC measurements, (b) Ni-based alloy salt and reference crucibles on the crucible holder of DSC.

2.4. Solubility Measurement and Salt-Metal Post-Analysis

To measure the solubilities of Na and Zn electrode metals in the selected molten salt electrolytes (NaCl-CaCl₂-BaCl₂ 37-45-18 mol%, NaCl-SrCl₂-KCl 30.0-26.5-43.5 mol%), the electrode metal was in direct contact with the electrolyte at the ALB's operating temperature (600 °C), and the solubility was measured versus the time of contact until saturation was reached. The tests were performed in an Ar inert environment (H₂O and O₂ < 1 ppm) inside the glovebox due to the salt mixture's strong hygroscopicity. As shown in Figure 4, a specialized setup (named HaloBat) was prepared for the tests. This experimental setup consists of (1) an oven, (2) a stainless steel (SS) crucible containing the molten salt, and (3) a thermocouple to control the salt temperature with a temperature regulator. A quartz sampler, as shown in Figure 4 was used to collect salt samples. The amount of dissolved electrode metal in the electrolyte salt mixture was then analyzed with titration by a commercial automatic titrator (Titrande, Metrohm, Filderstadt, Germany).

2.4.1. Na Solubility Measurement

The solubility of Na in selected molten salt electrolytes (NaCl-CaCl₂-BaCl₂ 37-45-18 mol%, NaCl-SrCl₂-KCl 30.0-26.5-43.5 mol%) at 600 °C was studied. Anhydrous salts with a purity of 99% were used for mixture preparation in the glovebox. The mole percent mixture ratio was converted to weight percent, and the balance was used to prepare 60 g of the required salt mixture inside the glovebox. The salt mixture was put into the SS

crucible and heated to 600 °C by the HaloBat. As shown in Figure 4, about 1 g Na metal was weighed and put into the inner steel tube after the salt mixture in the SS crucible was completely molten. The added Na metal was melted immediately and floated on the molten salt due to its lower density. After adding the Na metal, salt samples (of 2–4 g) were taken after every half to one hour to determine the change in the concentration of dissolved Na, which was measured with direct titration by the automatic titrator Titrand. The Na concentration steadily increases with time until a constant value (i.e., the solubility) is obtained for the point with the maximum amount of Na that can be dissolved in the salt.

For titration, the salt sample (1–2 g) was put in a sample beaker filled with 160 mL of demineralized water. Afterwards, the beaker was attached to the automatic titrator, and the impeller was used to completely dissolve the salt in the water to prepare the titration solution. During salt dissolution, all Na metal dissolved in the salt sample reacted with water to form sodium hydroxide according to the reaction $2\text{Na} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2$. The solution was directly titrated against hydrochloric acid (HCl 0.01 M) to get the equivalence point. Titration was automated by adjusting the dosing rate. At the equivalence point, the consumed volume of HCl (V_{HCl}) was recorded. The consumed HCl was equal to the molar amount of the NaOH in the titration solution, i.e., dissolved Na in the salt sample, according to the reaction $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$. Thus, V_{HCl} was used to calculate the concentration of dissolved Na with the following equation:

$$C_{\text{Na}} = \frac{V_{\text{HCl}} \times 0.01 \text{ mol/L}}{V_{\text{HCl}} \times 0.01 \text{ mol/L} + n_{\text{salt}}} \times 100 \quad (2)$$

where

C_{Na} represents the concentration of dissolved Na (mol%);

V_{HCl} is the consumed volume of HCl in L;

n_{salt} is the amount of the salt sample in mol.

The titration measurements on each salt sample were performed twice to ensure the accuracy of the result and get the average values and measurement error bars (standard deviation).

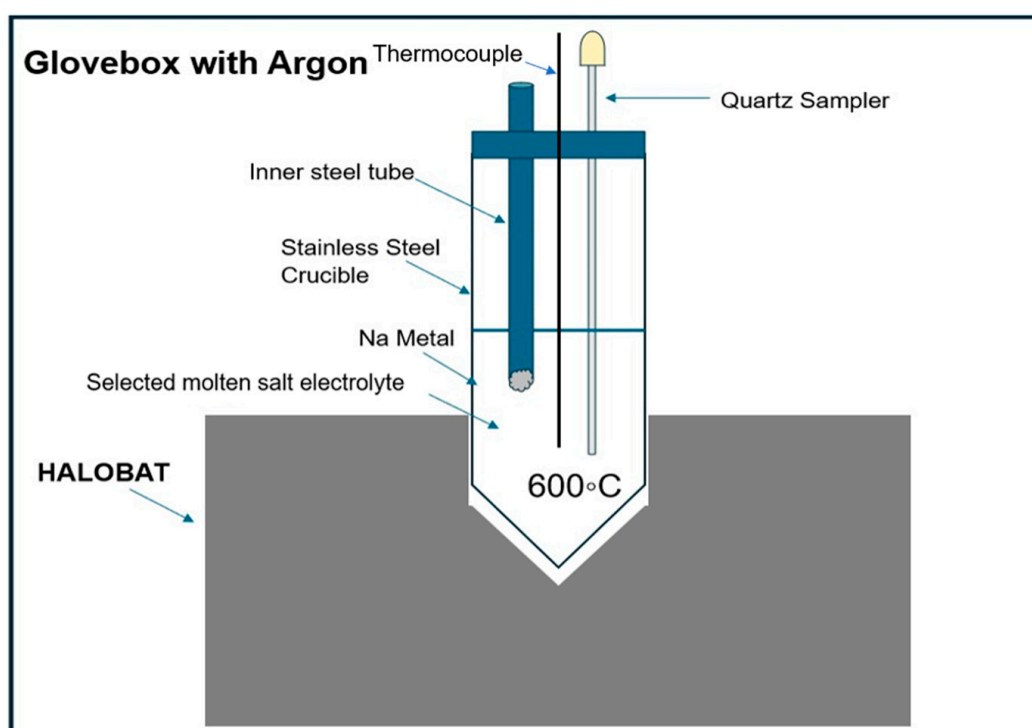


Figure 4. Schematic of setup with a Na metal holder (i.e., inner steel tube) for Na solubility measurements.

2.4.2. Zn Solubility Measurement

The solubility of Zn in selected molten salt electrolytes (NaCl-CaCl₂-BaCl₂ 37-45-18 mol%, NaCl-SrCl₂-KCl 30.0-26.5-43.5 mol%) at 600 °C was also studied. As for the Na solubility measurements, 60 g of the prepared salt mixture was put into the SS crucible and heated to 600 °C by the HaloBat setup. Different from the Na solubility measurements with the inner steel tube containing the floating Na, an alumina crucible was used to contain about 1 g Zn metal (see Figure 5) since liquid Zn has a higher density than the molten salt and good material compatibility with alumina (but not with SS). The alumina crucible with Zn was completely immersed in the molten salt after the salt was completely molten so that the Zn metal was in indirect contact with the molten salt. After that, salt samples (2-4 g) were taken every half to one hour to determine the concentrations of dissolved Zn by back titration.

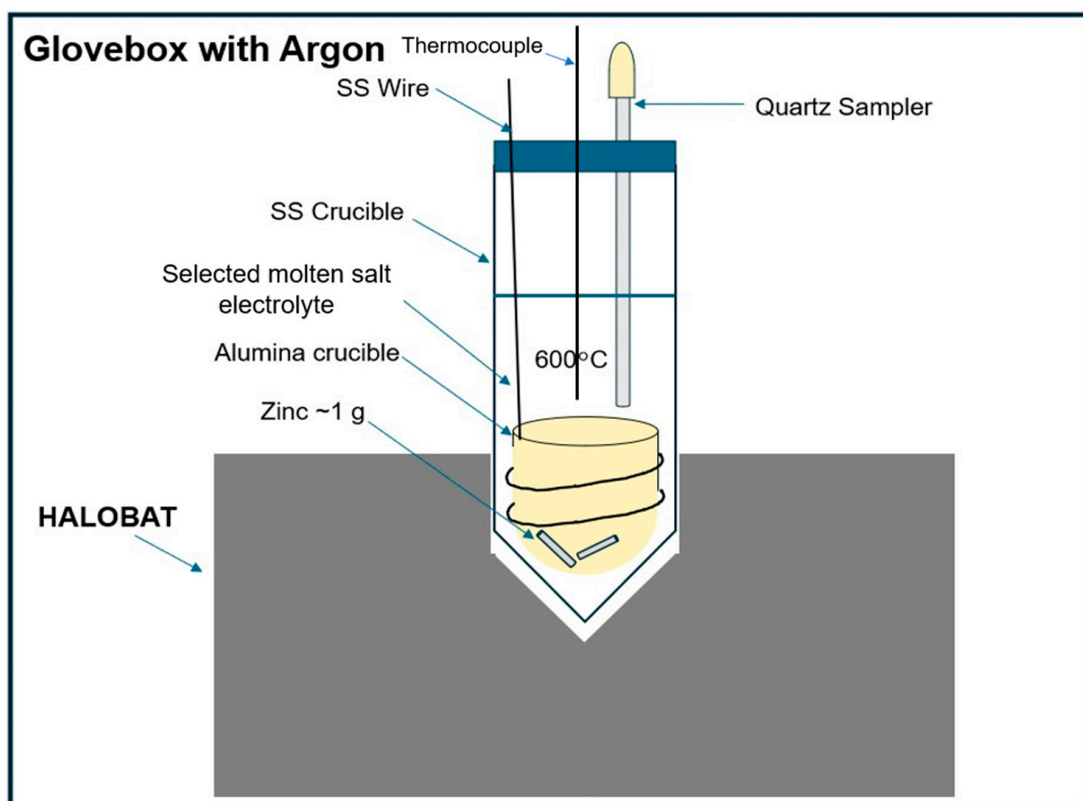


Figure 5. A schematic of the setup with a Zn metal holder (i.e., alumina crucible) for Zn solubility measurements.

For titration, the salt sample (1–2 g) was put in the sample beaker with 160 mL of demineralized water and 5 mL of 0.1 M HCl solution. The beaker was then attached to the automatic titrator, and the impeller was used to completely dissolve the salt in the water to prepare the titration solution. During the salt dissolution, all Zn metal dissolved in the salt sample reacted with HCl to form ZnCl₂ according to the reaction $\text{Zn} + 2\text{HCl} \rightarrow \text{ZnCl}_2 + \text{H}_2\text{O}$. The solution with excess HCl was back titrated with 0.1 M NaOH to get the equivalence point. Titration was automated by adjusting the dosing rate. At the equivalence point, the consumed volume of NaOH (V_{NaOH}) was recorded. The molar amount of dissolved Zn (n_{Zn} in mol) can be calculated with the following equation:

$$n_{\text{Zn}} = \frac{0.1 \text{ mol/L} \times 0.005 \text{ L} - 0.1 \text{ mol/L} \times V_{\text{NaOH}}}{2} \quad (3)$$

After that, n_{Zn} in mol was used to calculate the concentration of dissolved Zn with the following equation:

$$C_{Zn} = \frac{n_{Zn}}{n_{Zn} + n_{salt}} \times 100 \quad (4)$$

where C_{Zn} represents the concentration of dissolved Zn (mol%).

As for the Na samples, the titration Zn measurements of each salt sample were performed twice to ensure the accuracy of the result and to get the average values and measurement error bars (standard deviation).

3. Results and Discussion

3.1. FactSage Simulation

3.1.1. Binary Phase Diagrams

Figure 6 presents the binary system phase diagrams of NaCl with CaCl_2 , BaCl_2 , SrCl_2 , and KCl, which are simulated by FactSage. The phase diagrams show that the eutectic melting temperature of NaCl- CaCl_2 , NaCl- BaCl_2 , NaCl- SrCl_2 , and NaCl-KCl is about 506 °C, 650 °C, 560 °C, and 660 °C, respectively. The eutectic melting temperatures and salt compositions are summarized in Table 1. These simulated melting temperatures and melting behaviors (see, e.g., plot of c_p vs. T in Figure 7 (bottom) for eutectic NaCl- CaCl_2) agree well with the literature such as [32–35]. Comparison with the DSC measurement result on eutectic NaCl- CaCl_2 in Figure 7 (measured melting temperature of 502 °C for the eutectic NaCl- CaCl_2 48–52 mol%) also shows good agreement. Compared to BaCl_2 and KCl, the eutectic binary mixtures with CaCl_2 and SrCl_2 have much lower eutectic melting temperatures (below 600 °C). Thus, in this work, CaCl_2 and SrCl_2 are selected as the primary additives for NaCl to have a low melting temperature of the salt mixture as the ALB molten salt electrolyte. Since CaCl_2 could have a co-reduction issue and SrCl_2 could have the cost issue, BaCl_2 and KCl could be the third salt mixed to further reduce the melting temperature and/or material costs. The ternary phase diagrams studied will be presented in Section 3.1.2.

Table 1. A comparison of simulated eutectic temperatures and salt compositions of selected binary systems with those presented in the literature.

Binary System	Eutectic Temperature (°C)	Eutectic Composition (NaCl mol%)	Source
NaCl- CaCl_2	506	48%	This work
NaCl- CaCl_2	508	50%	[32]
NaCl- CaCl_2	500	48%	[33]
NaCl- BaCl_2	650	60%	This work
NaCl- BaCl_2	654	61%	[34]
NaCl- SrCl_2	560	48%	This work
NaCl- SrCl_2	560	48%	[35]
NaCl-KCl	660	50%	This work
NaCl-KCl	685	50%	[33]

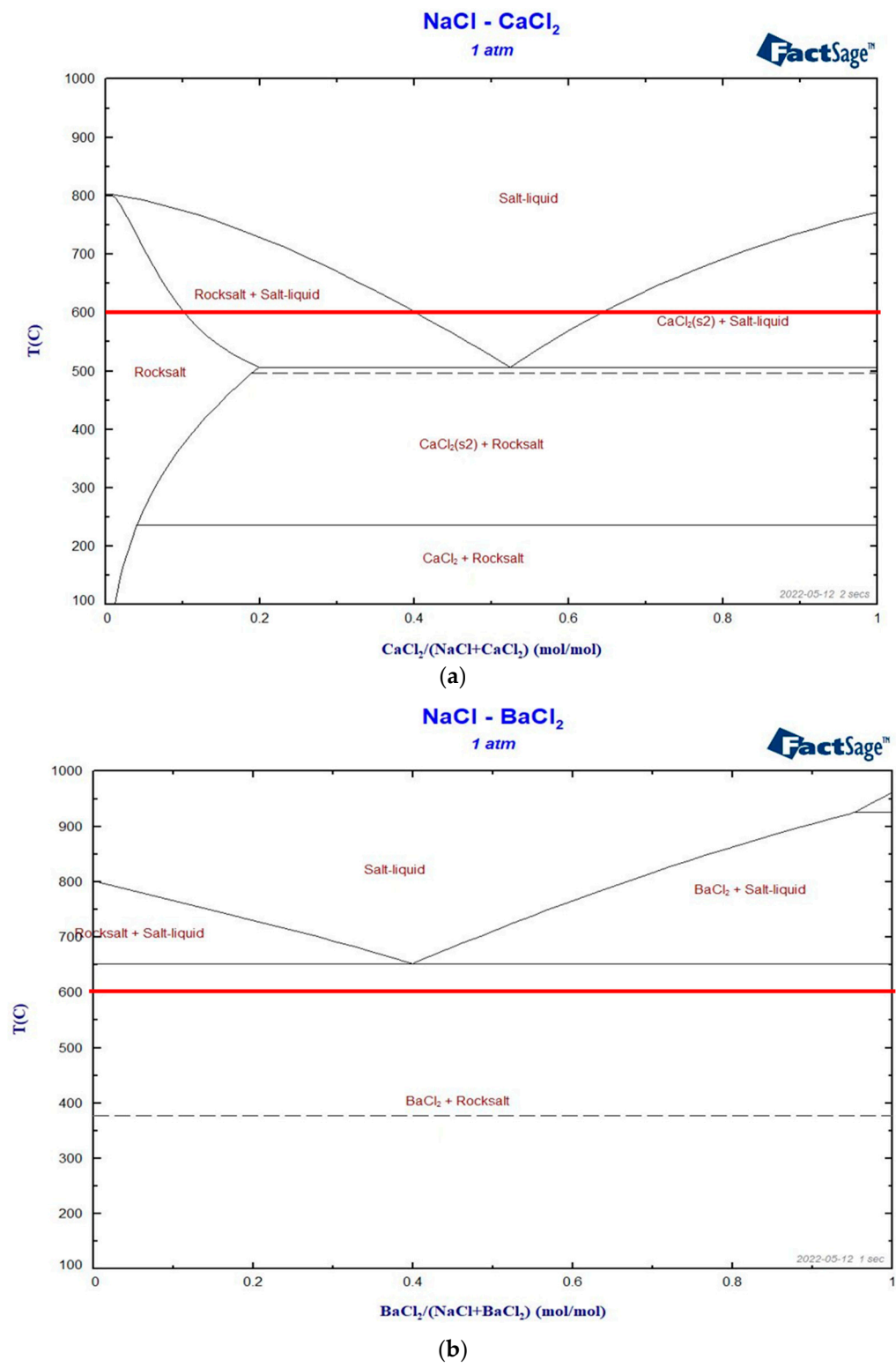


Figure 6. Cont.

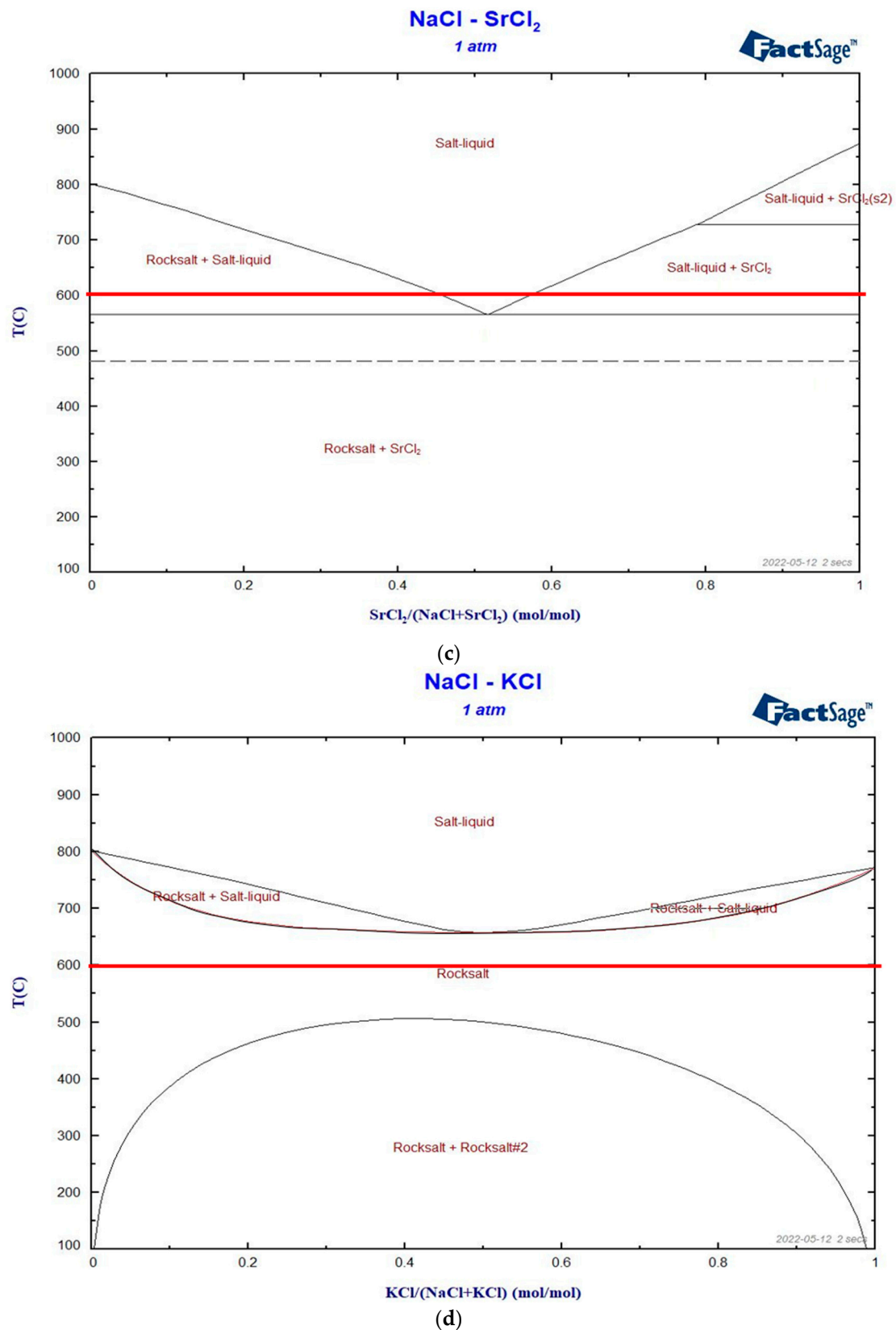


Figure 6. Simulated phase diagrams of (a) NaCl-CaCl₂, (b) NaCl-BaCl₂, (c) NaCl-SrCl₂, and (d) NaCl-KCl. The red lines show the expected ALB working temperature of 600 °C. The dotted lines in these simulated phase diagrams represent condensed phase boundaries calculated for high pressures when the gas phase does not appear.

3.1.2. Ternary Phase Diagrams

For the selected salts CaCl_2 , BaCl_2 , SrCl_2 , and KCl , all phase diagrams of the ternary salt systems with NaCl were also simulated with FactSage in this work. These five ternary systems ($\text{NaCl-CaCl}_2\text{-BaCl}_2$, $\text{NaCl-CaCl}_2\text{-SrCl}_2$, $\text{NaCl-CaCl}_2\text{-KCl}$, $\text{NaCl-SrCl}_2\text{-BaCl}_2$, and $\text{NaCl-SrCl}_2\text{-KCl}$) were selected for further investigation, whereas $\text{NaCl-BaCl}_2\text{-KCl}$ was not selected because of the high minimum melting temperatures of the NaCl-BaCl_2 and NaCl-KCl systems (see Section 3.1.1). NaCl is the necessary salt as the active electrode component, CaCl_2 and SrCl_2 are the primary additives, and BaCl_2 and KCl are the secondary additives to lower the melting temperature. All simulated ternary phase diagrams are shown in Figure 8. In the phase diagrams, the yellow areas in the phase diagrams represent the salt compositions with a melting temperature $\leq 600^\circ\text{C}$. The dark red line shows the salt composition change in the selected molten salt electrolyte for each studied ternary salt system during charging/discharging under the assumption of no co-reduction of the Na electrode. These molten salt electrolytes were selected according to the largest potential allowed change in the NaCl mol% (i.e., largest potential charge/discharge range of the ALB cell) when they should be kept in an all-liquid state at the representative ALB operating temperature of 600°C . The maximum and minimum allowed concentration of NaCl for $T_m \leq 600^\circ\text{C}$ (i.e., the largest potential charge/discharge range of the ALB cell) are pointed out with red and blue solid circles in the phase diagrams.

After comparing all the potential charge/discharge ranges, the $\text{NaCl-CaCl}_2\text{-BaCl}_2$ (53 mol% NaCl change allowed), $\text{NaCl-CaCl}_2\text{-SrCl}_2$ (56 mol% NaCl change allowed), and $\text{NaCl-SrCl}_2\text{-KCl}$ (47 mol% NaCl change allowed) are pre-selected as the promising molten salt electrolytes. For final selection, the comparison of EMFs (co-reduction issue) and material costs, as well as the solubilities of Na and Zn electrodes, will be presented in the following subsections.

Moreover, it is found that the midpoints of all the dark red lines between red and blue solid circles are very close to the minimum (eutectic) salt compositions of these studied ternary salt systems (pointed out with dotted red circles). All the minimum (eutectic) melting temperatures and corresponding salt compositions are summarized in Table 2. Since the molten salt electrolyte changes its composition in charge/discharge according to the dark red line in theory, for simplicity, the minimum (eutectic) salt compositions were used in the study on the material costs as well as the solubilities of Na and Zn electrodes for the final selection of the molten salt electrolytes.

Table 2. Simulated eutectic temperatures and salt compositions of selected ternary systems.

Ternary Systems	Min. Melting Temperature ($^\circ\text{C}$)	Eutectic Composition (mol%)	Source
$\text{NaCl-CaCl}_2\text{-BaCl}_2$	446	37.1-44.9-18.0	This work, FactSage
$\text{NaCl-CaCl}_2\text{-BaCl}_2$	454	37.1-44.9-18.0	This work, DSC
$\text{NaCl-CaCl}_2\text{-SrCl}_2$	448	37.7-40.4-21.9	This work, FactSage
$\text{NaCl-CaCl}_2\text{-SrCl}_2$	471	41.9-40.6-18.1	[35]
$\text{NaCl-CaCl}_2\text{-KCl}$	481	40.0-51.4-8.6	This work, FactSage
$\text{NaCl-CaCl}_2\text{-KCl}$	504	42-52-6	[34]
$\text{NaCl-SrCl}_2\text{-BaCl}_2$	555	45.6-43.0-11.4	This work, FactSage
$\text{NaCl-SrCl}_2\text{-KCl}$	503	30.0-26.5-43.5	This work, FactSage
$\text{NaCl-SrCl}_2\text{-KCl}$	503–505	30.0-26.5-43.5	This work, DSC

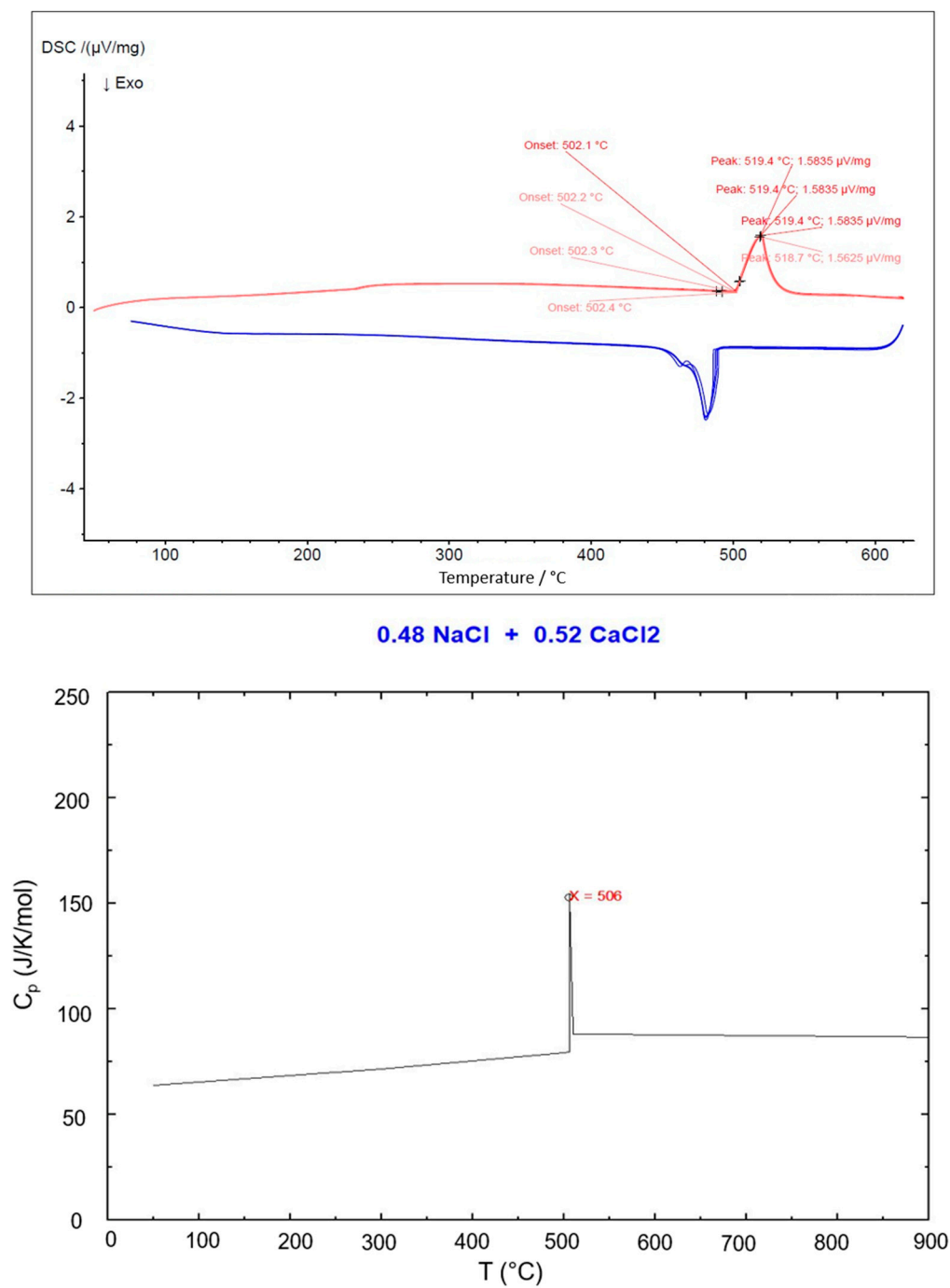


Figure 7. DSC test result for the eutectic NaCl-CaCl₂ 48–52 mol% (**top**) and simulated c_p vs. T via FactSage (**bottom**). The red and blue lines in the DSC test result represent the heating and cooling curves, respectively.

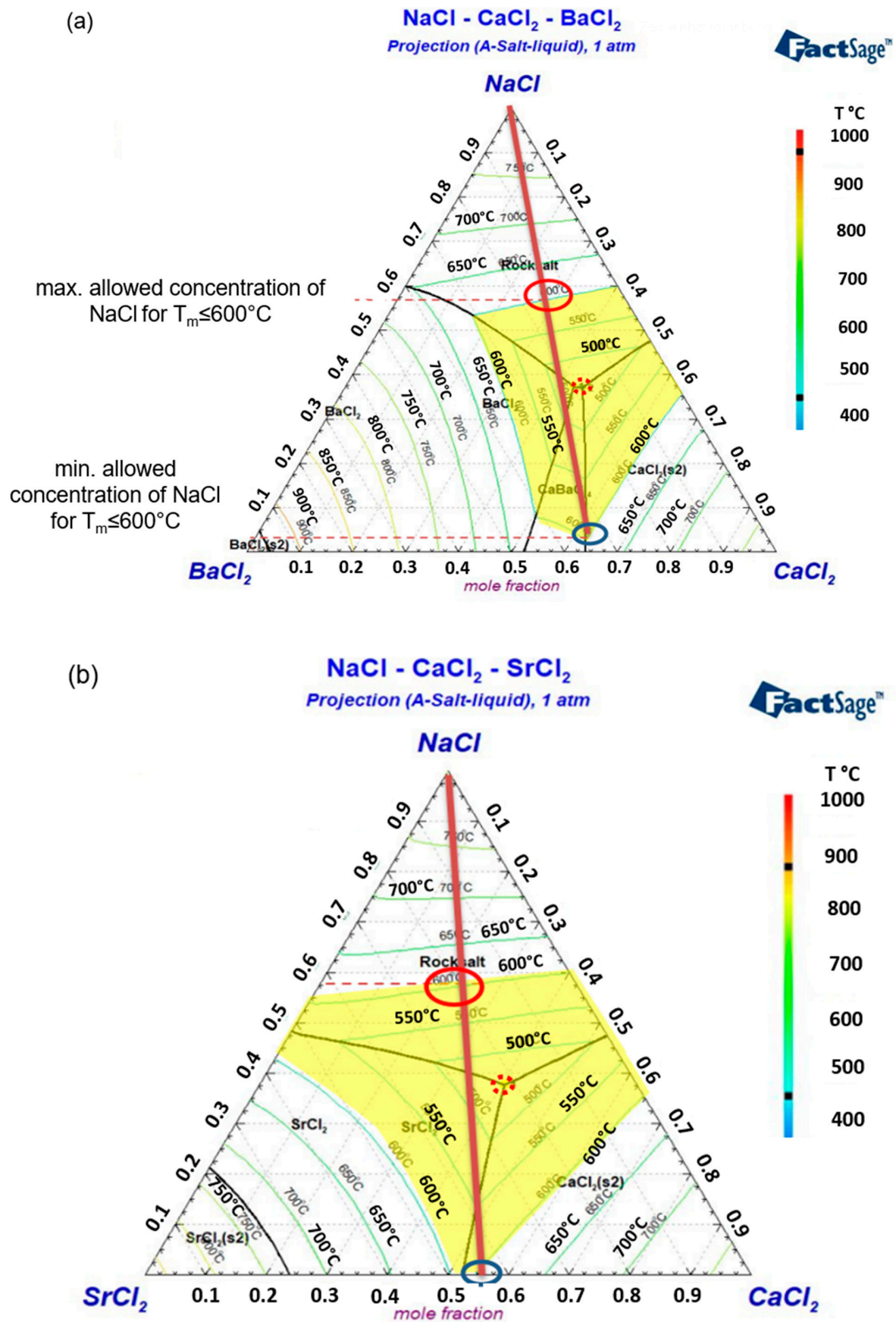


Figure 8. Cont.

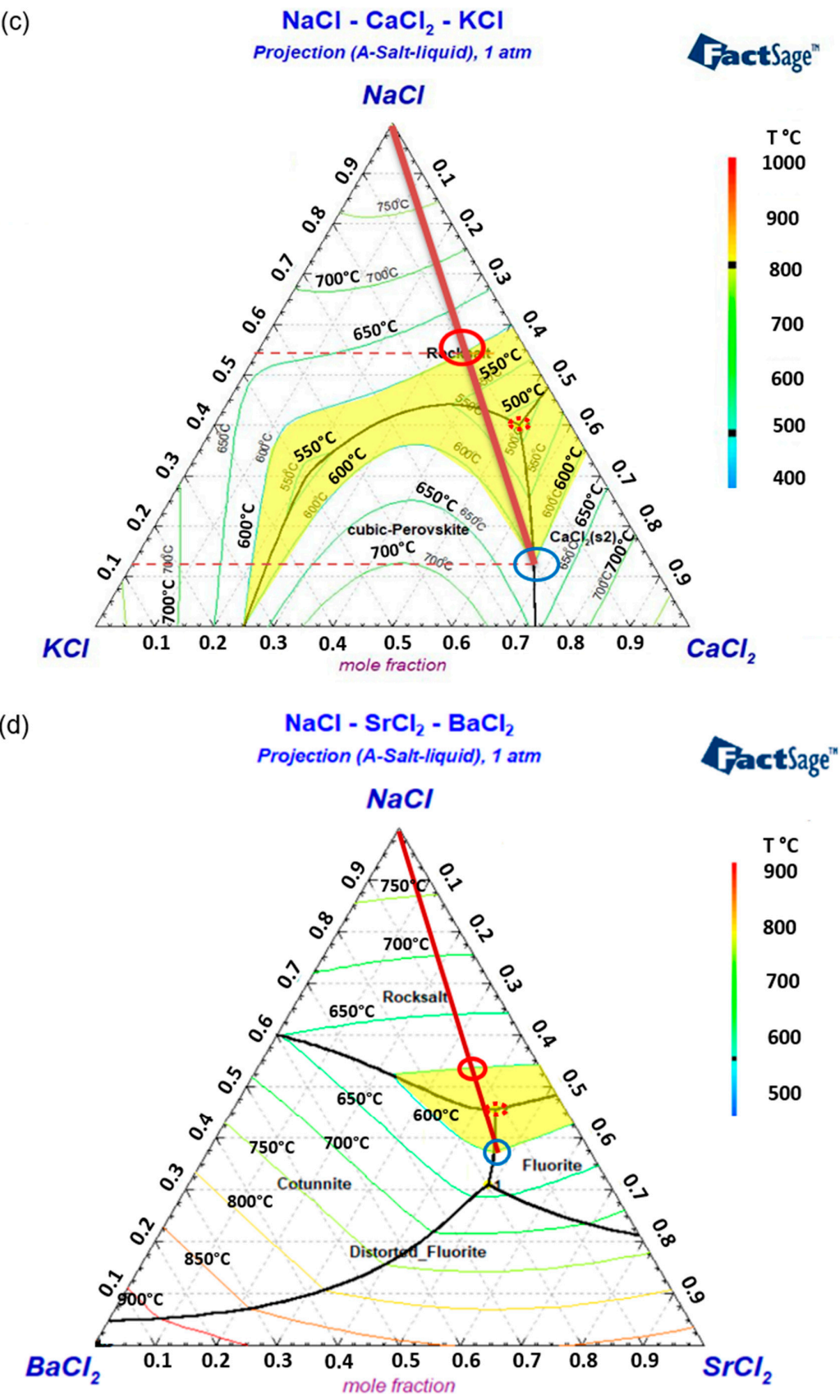


Figure 8. Cont.

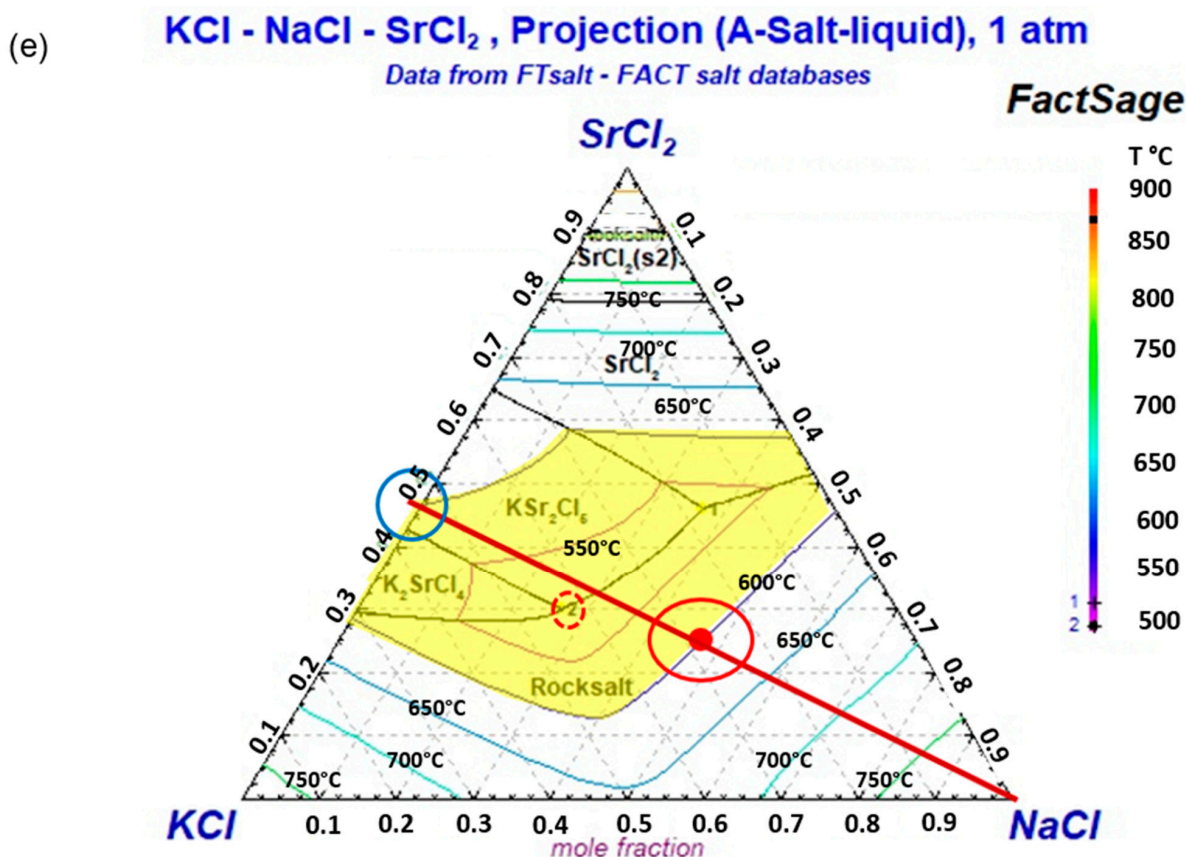


Figure 8. Simulated ternary phase diagrams: (a) NaCl-CaCl₂-BaCl₂, (b) NaCl-CaCl₂-SrCl₂, (c) NaCl-CaCl₂-KCl, (d) NaCl-SrCl₂-BaCl₂, and (e) NaCl-SrCl₂-KCl. Yellow areas in the phase diagrams represent the salt composition with a melting temperature not higher than 600 °C. Dark red lines show the changing salt composition during charging/discharging. The minimum temperature (eutectic) composition is pointed out with a red dotted circle. The maximum and minimum allowed concentrations of NaCl for $T_m \leq 600$ °C (i.e., the largest potential charge/discharge ranges of the ALB cell) are pointed out with red and blue solid circles in the phase diagrams.

3.2. Comparison of EMFs (Co-Reduction) and Material Costs

As mentioned above, to avoid the reactions of the salt with Na, only the chloride salts, whose electromotive forces (EMFs) are higher than Na/NaCl, can be used in the molten salt electrolyte. Moreover, the addition of more chloride salt with high EMFs in the molten salt electrolyte leads to less co-reduction during charging. One example of co-reduction is NaCl-CaCl₂ ($\text{Ca}^{2+} + 2\text{e}^- \rightarrow \text{Ca}$) because Ca has a similar EMF as Na (see Table 3). Thus, the theoretical EMFs of the selected chloride salts available in the literature [19] are compared. As shown in Table 3, the order of the theoretical EMF is $\text{BaCl}_2 > \text{KCl} > \text{SrCl}_2 > \text{CaCl}_2 \approx \text{NaCl}$ at 600 °C, while that of the cost is $\text{SrCl}_2 > \text{BaCl}_2 > \text{KCl} > \text{CaCl}_2 \gg \text{NaCl}$. Regarding the low material cost and large potential charge/discharge range, the pre-selected NaCl-CaCl₂-BaCl₂ salt mixture (eutectic salt mixture: 37.1-44.9-18.0 mol%, 0.32 USD/kg or 0.035 USD/mol) is the most promising ALB molten salt electrolyte (containing CaCl₂) but has the issues of Ca co-reduction and salt composition change as mentioned above, while the NaCl-SrCl₂-KCl salt mixture (eutectic salt mixture: 30.0-26.5-43.5 mol%, 0.61 USD/kg, or 0.056 USD/mol) could have a much smaller co-reduction issue due to high EMFs of SrCl₂ and KCl, a large potential charge/discharge range (see its phase diagram in Figure 8), and not high material cost. Thus, these two ternary systems are finally selected for further study via DSC, melting behavior, and performance in test cells.

Table 3. A comparison of theoretical EMFs of metal chlorides at 600 °C [19] and their large-scale costs [26].

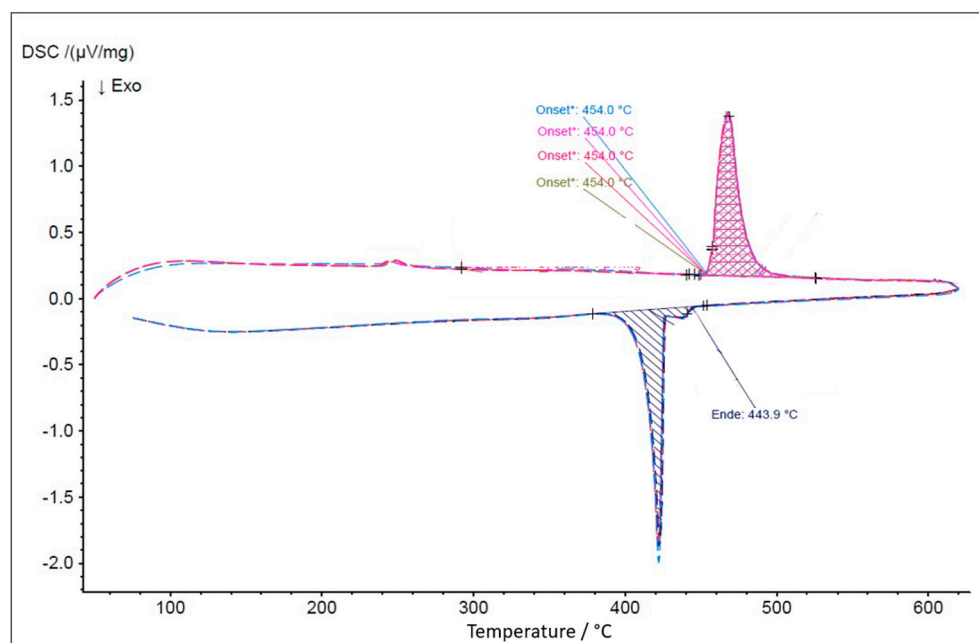
Metal Chlorides	EMF (V) at 600 °C	Cost (USD/kg)
BaCl ₂	3.728	~0.5
KCl	3.658	~0.4
SrCl ₂	3.612	~1 *
CaCl ₂	3.462	~0.3
NaCl	3.424	~0.06

* Common large-scale commercial price from [Alibaba.com](https://www.alibaba.com).

3.3. DSC Measurements and Simulated c_p vs. T

3.3.1. NaCl-CaCl₂-BaCl₂

The simulated melting temperature of the eutectic NaCl-CaCl₂-BaCl₂ (37.1-44.9-18.0 mol%) was verified with DSC measurement. The DSC curve in Figure 9 (top) shows that only one peak is observed when heating to above 600 °C, which agrees well with the simulated c_p vs. T plot in Figure 9 (bottom), while only a small secondary peak exists in addition to the main peak when cooling to room temperature. This means that the salt mixture is almost eutectic. The melting temperature of the salt mixture is 454 °C (heating), which agrees with the simulated value of 446 °C by FactSage in Figure 9 (bottom). Such a low-melting-temperature and low-cost salt mixture (0.32 USD/kg) is promising as a molten salt electrolyte for ALB, and the NaCl-CaCl₂-BaCl₂ molten salt electrolyte is suggested to be used in the ALB test cell and the ALB demonstrators under development.

**Figure 9.** Cont.

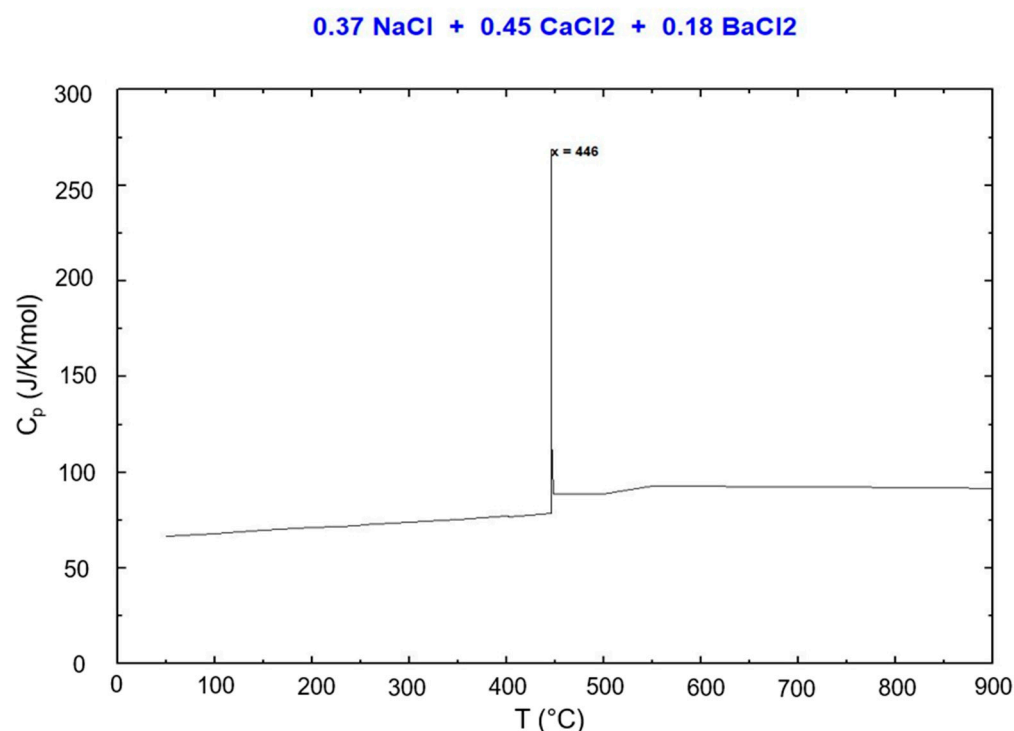


Figure 9. DSC result (**top**) and simulated c_p vs. T (**bottom**) for the eutectic NaCl-CaCl₂-BaCl₂ (37.1-44.9-18.0 mol%).

3.3.2. NaCl-SrCl₂-KCl

The melting temperature and behavior of the simulated eutectic NaCl-SrCl₂-KCl (30.0-26.5-43.5 mol%) were also verified using the DSC measurement. The DSC curve in Figure 10 shows that only one peak (but not ideal) is observed when heating to above 600 °C and, also, when cooling to room temperature. During the cooling, the melting peaks increase sharply and at varying temperatures, which can be assigned to the subcooling phenomenon. This means that the salt mixture is almost eutectic. The melting temperature of the salt mixture is 503–505 °C (heating), which agrees well with the simulated value of 503 °C shown in the ternary phase diagram (Table 2) and also with the simulated c_p vs. T (not presented in this work). Such a low-melting-temperature salt mixture is promising as a molten salt electrolyte for ALB. Compared to NaCl-CaCl₂-BaCl₂, the NaCl-SrCl₂-KCl molten salt electrolyte has less of a co-reduction issue due to high EMFs, and thus, it is also strongly suggested that it be used in the ALB test cell and the ALB demonstrators under development.

3.4. Solubilities of Metal Electrodes in Selected Molten Salt Electrolytes

3.4.1. Solubilities of Na Metal

Figure 11 shows the concentrations of dissolved Na in selected NaCl-CaCl₂-BaCl₂ (37.1-44.9-18.0 mol%) molten salt electrolyte at 600 °C with measurement error vs. time. In the first 5 h, the concentration of dissolved Na rapidly increases with time. After 24 h, the concentration of dissolved Na reaches the solubility limit in NaCl-CaCl₂-BaCl₂ (i.e., saturation concentration of dissolved Na). For all the measured concentrations, the measurement errors are smaller than 0.015 mol%, which is small compared to the concentrations of dissolved Na. The Na solubility in the selected NaCl-CaCl₂-BaCl₂ molten salt electrolyte at 600 °C is around 1.2 mol%.

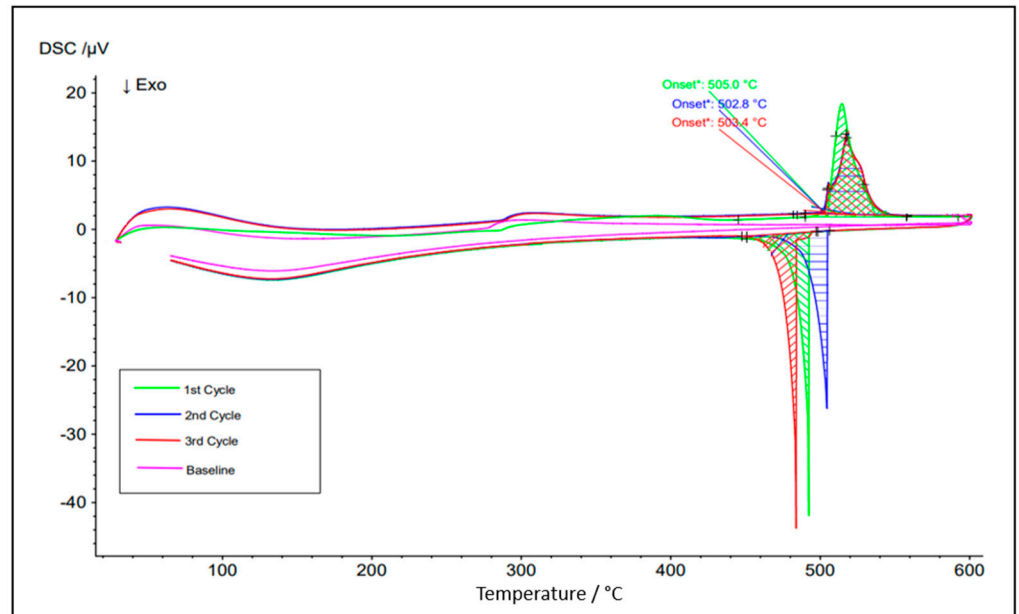


Figure 10. DSC result for the eutectic NaCl-SrCl₂-KCl (30.0-26.5-43.5 mol%).

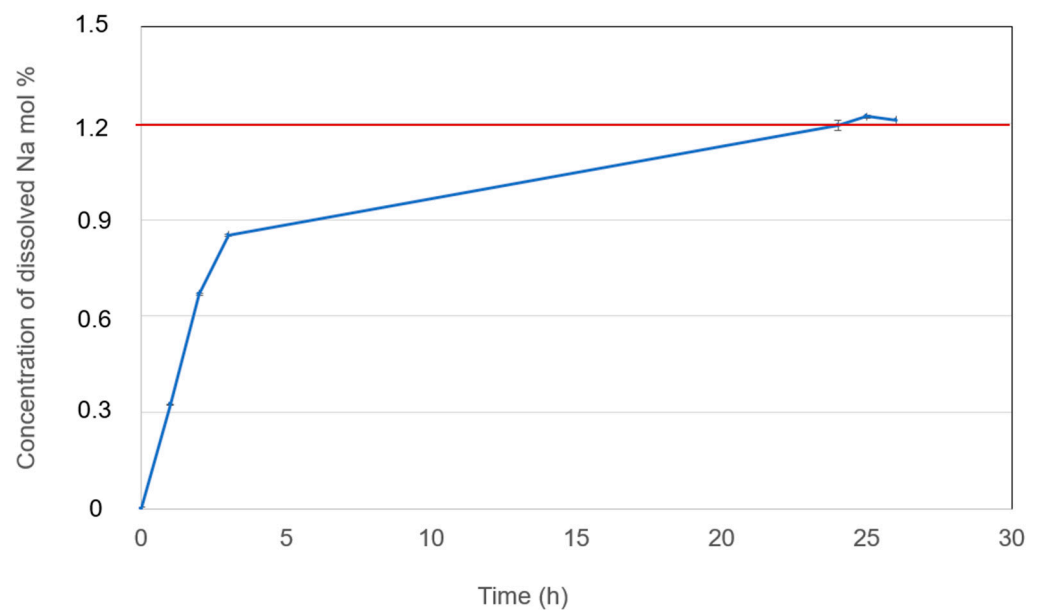


Figure 11. Dissolved Na metal in selected NaCl-CaCl₂-BaCl₂ (37.1-44.9-18.0 mol%) molten salt electrolyte at 600 °C with measurement error bar versus time. The measurement error bars are very small compared to the concentrations of dissolved Na. The red line represents the solubility of Na, i.e., the maximum concentrations of dissolved Na in the molten salt.

Figure 12 shows the change in the concentrations of dissolved Na in selected NaCl-SrCl₂-KCl (30.0-26.5-43.5 mol%) molten salt electrolyte at 600 °C with measurement error vs. time. In the first 2.5 h, the concentration of dissolved Na increases fast to 0.15 mol%. After 18 h, the concentration of dissolved Na reaches the saturation of about 0.22 mol%, i.e., the Na solubility in the selected NaCl-SrCl₂-KCl molten salt electrolyte at 600 °C is around 0.22 mol%, much lower than that in another selected NaCl-CaCl₂-BaCl₂ molten salt electrolyte.

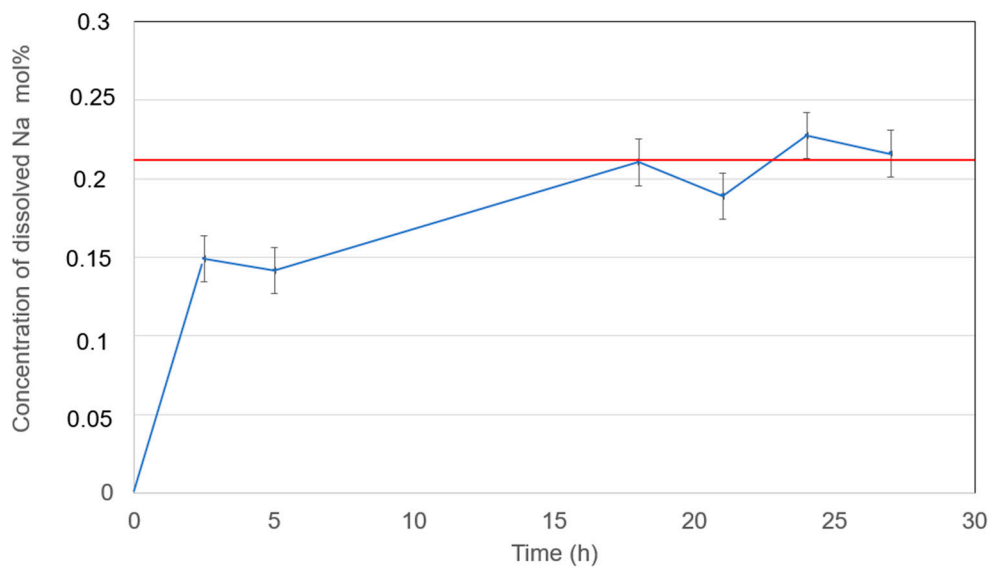


Figure 12. Dissolved Na metal in selected NaCl-SrCl₂-KCl (30.0-26.5-43.5 mol%) molten salt electrolyte at 600 °C with measurement error bar versus time. The red line represents the solubility of Na, i.e., the maximum concentrations of dissolved Na in the molten salt.

To the best of our knowledge, previous work on Na solubilities in NaCl, SrCl₂, and KCl is generally limited. As shown in Table 4, the determined Na solubilities in the selected molten salt electrolytes are compared with the literature [17,27,36]. As mentioned in the review paper of MIT on liquid metal batteries [27], the Na solubility in molten NaCl is 2.1 mol% at 795 °C. In our previous work, the Na solubility in LiCl-NaCl-KCl (59-5-36 mol%) is 0.09 and 0.15 mol% at 450 °C and 560 °C, respectively [17]. If the temperature is extended to 600 °C using the activation energy of Na dissolution in this molten salt, the Na solubility in LiCl-NaCl-KCl (59-5-36 mol%) is 0.18 mol%. The Na solubility in eutectic NaCl-CaCl₂ molten salt at 600 °C is about 3.3 mol% [36]. In summary, Na has a similar high solubility in NaCl-CaCl₂-BaCl₂ (37.1-44.9-18.0 mol%) as the eutectic NaCl-CaCl₂, and a similar low solubility in NaCl-SrCl₂-KCl (30.0-26.5-43.5 mol%) as e.g., LiCl-NaCl-KCl (59-5-36 mol%), at the studied operating temperature of ALB (600 °C).

Table 4. Comparison of Na solubilities in molten chlorides obtained in this work and available in the literature.

Molten Chlorides	Na Solubility (mol%)	Source
NaCl-CaCl ₂ -BaCl ₂ (37.1-44.9-18.0 mol%)	1.2 (600 °C)	This work
NaCl-SrCl ₂ -KCl (30.0-26.5-43.5 mol%)	0.22 (600 °C)	This work
NaCl-CaCl ₂ (eutectic)	~3.3 (600 °C)	[36]
NaCl	2.1 (795 °C)	[27]
LiCl-NaCl-KCl (59-5-36 mol%)	0.09 (450 °C), 0.15 (560 °C), 0.18 (600 °C)	[17]

As concluded in the literature [17,18,27], the self-discharge of the liquid metal—molten salt batteries is strongly related to the dissolution of metal electrodes (e.g., Na) into the molten salt electrolytes (i.e., solubilities of metal electrodes in the molten salt electrolytes and dissolution/reaction kinetics). Regarding the high Na solubility in NaCl-CaCl₂-BaCl₂, which could enhance the self-discharge of the ALB, it is suggested to give special attention when using this molten salt electrolyte.

3.4.2. Solubilities of Zn Metal

Figure 13 shows the concentrations of dissolved Zn in the selected NaCl-CaCl₂-BaCl₂ (37.1-44.9-18.0 mol%) molten salt electrolyte at 600 °C with measurement error vs. time. In the first hour, the concentration of dissolved Zn rapidly increases with time to 0.04 mol%. After that, the concentration of dissolved Zn reaches the solubility limit (i.e., saturation concentration of dissolved Zn). The measurement errors are about 0.01 mol%. The Zn solubility in the selected NaCl-CaCl₂-BaCl₂ molten salt electrolyte at 600 °C is around 0.04 mol%.

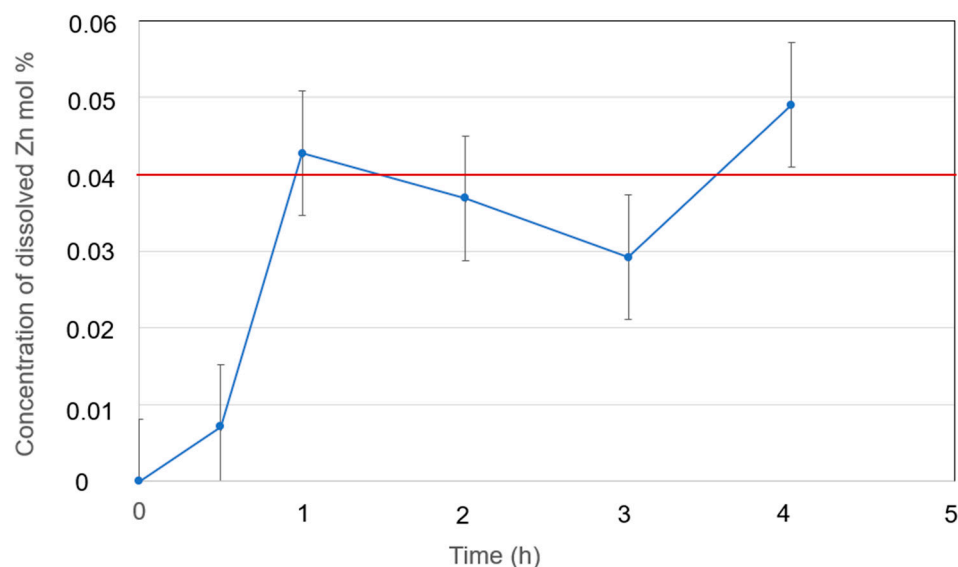


Figure 13. Dissolved Zn metal in eutectic NaCl-CaCl₂-BaCl₂ (37.1-44.9-18.0 mol%) at 600 °C with measurement error bar versus time. The red line represents the solubility of Zn, i.e., the maximum concentrations of dissolved Zn in the molten salt.

Figure 14 shows the concentrations of dissolved Zn in the selected NaCl-SrCl₂-KCl (30.0-26.5-43.5 mol%) molten salt electrolyte at 600 °C with measurement error vs. time. In the first hour, the concentration of dissolved Na increases to 0.05 mol%. After that, the concentration of dissolved Zn reaches saturation. Thus, the Na solubility in the selected NaCl-SrCl₂-KCl molten salt electrolyte at 600 °C is around 0.05 mol%, similar to that in the other selected NaCl-CaCl₂-BaCl₂ molten salt electrolyte.

The data on Zn solubilities in molten chlorides available in the literature are very limited. Thus, the determined Zn solubilities in the two selected molten salt electrolytes are compared to the Zn and Mg solubilities in molten salts available in the literature [27,37] (see Table 5). Corbett et al. measured the solubilities of Zn metal in pure molten ZnCl₂ and ZnI₂, which are 0.61 and 0.87 mol% at 600 °C, respectively [37]. As mentioned in the review paper on liquid metal batteries [27], the Mg solubility in molten MgCl₂ is 0.20-1.2 mol% at 714–900 °C (0.87 mol% at 800 °C). If the temperature is extended to 600 °C using the activation energy of Mg dissolution in this molten salt, the Mg solubility in molten MgCl₂ is 0.07 mol%. Thus, it is concluded that the Zn solubilities in the selected molten salt electrolytes for ALB determined in this work are comparable with the Zn and Mg metal solubilities in chlorides, limitedly available in the literature.

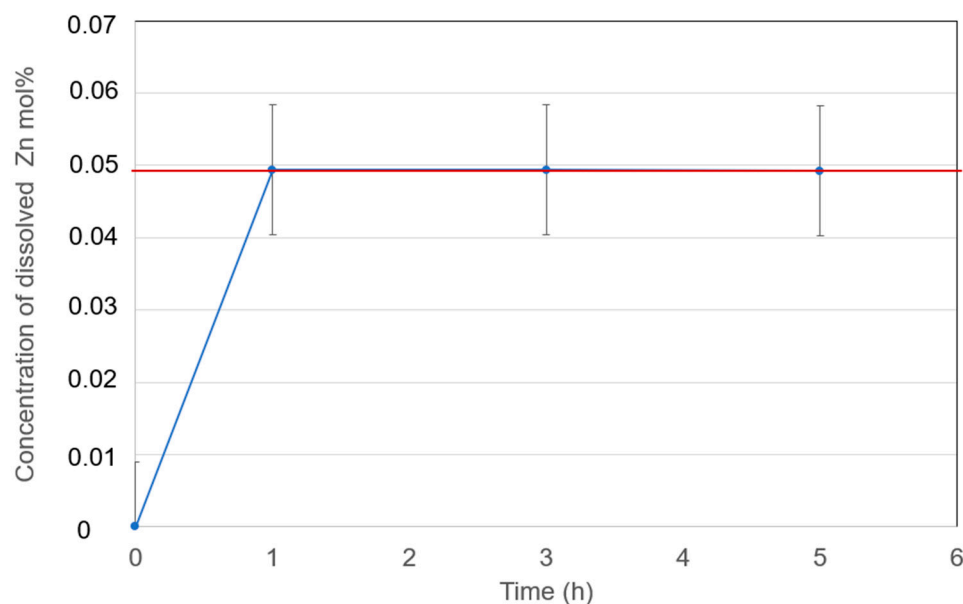


Figure 14. Dissolved Zn metal in eutectic NaCl-SrCl₂-KCl (30.0-26.5-43.5 mol%) at 600 °C with measurement error bar versus time. The red line represents the solubility of Zn, i.e., the maximum concentrations of dissolved Zn in the molten salt.

Table 5. A comparison of Zn solubilities in molten salts obtained in this work and available in the literature and Mg solubilities in molten salts available in the literature.

Metal in Molten Salts	Metal Solubility (mol%)	Source
Zn in NaCl-CaCl ₂ -BaCl ₂ (37.1-44.9-18.0 mol%)	0.04 (600 °C)	This work
Zn in NaCl-SrCl ₂ -KCl (30.0-26.5-43.5 mol%)	0.05 (600 °C)	This work
Zn in ZnCl ₂	0.187 (498 °C), 0.61 (600 °C)	[37]
Zn in ZnI ₂	0.28 (498 °C), 0.87 (600 °C)	[37]
Mg in MgCl ₂	0.20–1.2 (714–900 °C), 0.07 (600 °C)	[27]

Compared to the solubilities of Na in the two selected molten salt electrolytes of ALB determined in this work, the solubilities of Zn are lower. This means that, compared to the Na electrode, less attention needs to be paid to the Zn electrode for self-discharge due to its much lower solubility in the molten salt electrolyte.

4. Conclusions

In this work, the chlorides CaCl₂, BaCl₂, SrCl₂, and KCl are selected to form a low-melting-temperature salt mixture with NaCl as a molten salt electrolyte for Na-ZnCl₂ ALBs. The selection of the molten salt electrolyte is based on various criteria, including high electromotive force (EMF) for a small co-reduction issue, low melting temperature for a large charge/discharge range, low solubilities of Na and Zn electrodes for low self-discharge, low material costs, and high material abundance for easy scaling-up. The main conclusions and suggested future works are summarized as follows:

- Binary and ternary phase diagrams of these molten salt mixtures were simulated via FactSage, and some selected salt compositions were verified by DSC. Based on the melting temperatures obtained from the binary phase diagrams, CaCl₂ and SrCl₂ are selected as the primary additives for NaCl. CaCl₂ could have a co-reduction issue with the Na electrode due to a similar EMF as NaCl. SrCl₂ is more expensive than other chlorides. BaCl₂ and KCl are the third salt mixed to further reduce the co-reduction issue, melting temperature, and/or material costs.
- Regarding the low material cost and melting temperature, the NaCl-CaCl₂-BaCl₂ (0.32 USD/kg) is one of the most promising ALB molten salt electrolytes, but the

co-reduction of Ca in the Na electrode could be an issue that should be examined in future work. The NaCl-SrCl₂-KCl is expected to have the least co-reduction issue due to high EMFs. However, it has a higher melting temperature and higher cost (0.61 USD/kg) due to the utilization of SrCl₂. Thus, the eutectic mixtures of these two ternary systems were selected for further study via DSC and melting behavior.

- Melting temperatures and melting behaviors of eutectic NaCl-CaCl₂-BaCl₂ (eutectic 37.1-44.9-18.0 mol%, $T_{\text{eut}} = 446\text{ }^{\circ}\text{C}$) and NaCl-SrCl₂-KCl (eutectic 30.0-26.5-43.5 mol%, $T_{\text{eut}} = 503\text{ }^{\circ}\text{C}$) were verified by DSC measurement and c_p vs. T simulation of FactSage. The measured melting temperatures agree with the simulated values well. This means that FactSage simulation could be used to assist further optimization of the molten salt electrolyte (e.g., optimized salt composition) and the overall cell designs. In future work, DSC measurements on more salt compositions at various states of charge of the cell will be performed based on the results from the cell tests, such as electrochemical performance, and from neutron imaging of the operating cell, such as salt phase changes.
- Na- and Zn solubilities in these two selected molten salt electrolytes (NaCl-CaCl₂-BaCl₂ 37-45-18 mol%, NaCl-SrCl₂-KCl 30.0-26.5-43.5 mol%) at 600 °C were investigated with a homemade setup in the glovebox and an analysis method based on titration. To the best of our knowledge, these data are available in the literature for the first time.
- The Na solubilities in the eutectic NaCl-CaCl₂-BaCl₂ and NaCl-SrCl₂-KCl molten salt electrolyte at 600 °C is 1.2 mol% and 0.22 mol%, respectively. Such high Na solubility in NaCl-CaCl₂-BaCl₂ can enhance the self-discharge of ALBs, which deserves special attention. For NaCl-SrCl₂-KCl, the Na solubility is low.
- Zn solubilities in the eutectic NaCl-CaCl₂-BaCl₂ and NaCl-SrCl₂-KCl molten salt electrolyte at 600 °C are 0.04 mol% and 0.05 mol%, respectively. Compared to Na, Zn has much lower solubility in the examined molten chlorides. Thus, the Zn solubility is likely not an important factor for self-discharge.
- It is suggested to pay more attention to the reaction of Na with ZnCl₂ in the molten salt at the interface between Na metal and the molten salt electrolyte, which has been reported in the literature [7] and can lead to fast self-discharge. It is suggested for future work to find the solutions to prevent fast self-discharge, e.g., finding and using a good-performance diaphragm.
- Overall, the NaCl-CaCl₂-BaCl₂ and NaCl-SrCl₂-KCl salt mixtures are selected in this work and are considered the two most promising electrolytes for Na-ZnCl₂ ALB. The NaCl-CaCl₂-BaCl₂ (eutectic 37.1-44.9-18.0 mol%) and NaCl-SrCl₂-KCl (eutectic 30.0-26.5-43.5 mol%) molten salt electrolytes are suggested to be tested in the ALB demonstrators.
- Future work is suggested on optimization of the molten salt electrolyte by adding some NaCl in these two selected molten salt electrolytes for a larger operation range of the ALB cell based on the ternary phase diagrams obtained in this work and the cell tests.

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