An electrolysis-displacement-distillation approach for production of Li, Mg, Ca, Sr, and Ba metals

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Abstract

Green metal-electrode batteries call for the clean production of s-block metals. Herein, we develop an electrolysis-displacement-distillation (EDD) approach to producing s-block metals with low-carbon emissions and no chlorine gas evolution. The clean production stems from the choice of a molten NaCl-Na₂CO₃ electrolyte to prevent chlorine gas evolution, an inert nickel-based anode to produce oxygen, and a liquid metal cathode to make the cathodic product (e.g., Na-Sn) sit at the bottom of the electrolytic cell. Later, M-Sn (M = Li, Mg, Ca, Sr, and Ba) alloys are successfully prepared by a displacement reaction between the Na-Sn alloy and molten NaCl-LiCl, NaCl-MgCl₂, NaCl-CaCl₂, NaCl-SrCl₂, or NaCl-BaCl₂ with a displacement efficiency of >96.0%. Further, Li, Mg, Ca, Sr, and Ba metals are separated from M-Sn alloys using the vacuum distillation with a separation rate of >95.0%. We achieve a current efficiency of 81.0% for the electrolytic production of 100 kg of liquid Na-Sn alloy, which holds the promise to produce s-block metals at a large scale.

Keywords

molten salt electrolysis, liquid Sn cathode, displacement, vacuum distillation, s-block metals
1. Introduction

The invention of voltaic pile in 1799 by Alessandro Volta allowed Humphry Davy to conduct the electrolysis of salts or caustic soda, which leads to the discovery of s-block metals as well as empowering the rapid development of modern electrochemistry\textsuperscript{1-4}. S-block metals are playing an indispensable role in advancing the modernization of our society such as metallurgy, chemistry, energy storage, automobile, aerospace, and atomic energy sectors\textsuperscript{5-9}. With the development and application of high-energy metal batteries such as metal-ion batteries and metal-anode batteries in recent years, the global demand for s-block metals is increasing year by year\textsuperscript{10-13}. However, the ever-increasing production of s-block metals will cause significant environmental burdens\textsuperscript{14-16}.

There are two principal routes for the industrial production of s-block metals: the electrolytic and thermal reduction routes\textsuperscript{17-20}. The electrolytic method was first deployed using the molten salt electrolyte that had a wide electrochemical window to allow the deposition of s-block metals while generating toxic and corrosive chlorine gas (Cl\textsubscript{2}). Scientific advances have been made in the field of high-temperature molten-salt electrochemistry for clean metal extraction\textsuperscript{21-26}. Later, the success of the aluminum smelter (Hall–Héroult cell) brought Al products into our daily life. In the Hall–Héroult cell, molten cryolite dissolves Al\textsubscript{2}O\textsubscript{3} that is then being electrochemically split to liquid Al at the bottom cathode and CO\textsubscript{2} at a carbon anode. The deployment of the Hall–Héroult cell greatly reduced the Al price so that Al products have become widespread commodities in our daily life\textsuperscript{3,27}. Hence, scientists have tried to copy this method to
produce s-block metals.

However, several issues exist in different systems. For the extraction of Na, the relatively high Na solubility in molten NaCl (melting point: 801 °C) forces people to use molten NaCl-CaCl$_2$ to decrease the operating temperature$^{28}$. However, the inclusion of CaCl$_2$ precludes the use of oxide-containing species in order to avoid the production of CO$_3^{2-}$ that can be reduced to carbon at the cathode that competes with the Na deposition. Carbon deposition issues are also faced for the extraction of Li, Ca, Sr, and Ba in the molten chloride-oxide systems equipped with a carbon anode$^{29-31}$. As a consequence, the electrolysis should be conducted in oxide-free molten chloride in which pure Li, Na, Ca, Sr, and Ba are generated at the cathode and Cl$_2$ is generated at the carbon anode$^{3,28,32}$. However, the great amount of by-product Cl$_2$ is inevitably generated which brings some problems: First, the Cl$_2$ will decrease current efficiency because no ion-exchange membrane is available in the high-temperature chloride system. Second, it is difficult to make a gas-tight high-temperature electrolyzer, so that the leakage of Cl$_2$ is a risk to workers and residents nearby. Third, it is difficult to cool the hot gases which usually include some salt vapors that will block the pipelines. Fourth, the collected Cl$_2$ contains impurities and needs to be purified before use. For Mg, there is no carbon deposition issue because CO$_3^{2-}$ is thermodynamically unstable in molten MgCl$_2$.$^3$ However, the solubility of MgO is low in oxide-free MgCl$_2$-based molten salts, thereby the MgCl$_2$ system is adopted. For the electrolysis of MgCl$_2$-based salts, the electrolyzer requires clean and anhydrous MgCl$_2$ that is usually obtained from the mineral through a series of tedious and energy-intensive processes (leaching,
purification, filtration, and dehydration). Coupled with the problems posed by Cl₂, these combinations made molten MgCl₂ electrolysis economically prohibitive and gradually been replaced by thermal reduction process in the 2000s. Although the Pidgeon process is dominating the industrial production of Mg, this thermal reduction process produces huge amounts of solid wastes and CO₂ (~45.2 kg CO₂ per kg Mg) resulting from roasting minerals (dolomite, CaCO₃·MgCO₃), heating, and the consumption of ferrosilicon (Fe-Si) whose production generates CO₂ by the carbothermic reduction. Thus, we need to develop novel ways to avoid the generation of Cl₂ and reduce the generation of CO₂ and energy consumption for the production of s-block metals.

Here, we develop an electrolysis-displacement-distillation (EDD) approach to preparing pure Li, Mg, Ca, Sr, and Ba metals without generating Cl₂ (Fig. 1), replacing the high CO₂ emission and energy consumption of the thermal reduction process. First, the use of liquid metal electrodes accommodates electrolytic liquid Na, thereby avoiding liquid Na flowing on the top of salt as well as suppressing the dissolution of Na metal in molten salt. And the use of Na₂CO₃ salt prevents the generation of Cl₂ at the anode. Second, the electrolytic liquid Na-Sn alloy can reduce MClₙ in molten NaCl-MClₙ (M refers to Li, Mg, Ca, Sr, Ba, n is the valence of the metal cations) to produce M-Sn alloys, which is driven by the potential difference between Na-Sn alloy and M-Sn alloys. Finally, since the vapor pressure of M metals is several orders of magnitude higher than that of Sn metal, M metals can be separated by vacuum distillation from displaced M-Sn alloys. In addition, this technology can also be used to prepare various reactive metals such as transition metals and rare earth metals.
2. Experimental procedures

2.1. Preparation of liquid Na-Sn alloy by molten Na$_2$CO$_3$-NaCl electrolysis

Liquid Na-Sn alloy was prepared by a two-electrode system (Fig. 2). The mixture of Na$_2$CO$_3$ (Anhydrous, 99.9%, Sinopharm) and NaCl (Anhydrous, 99.9%, Sinopharm) with a eutectic composition was used as the electrolyte, and high-purity Sn (Ingot, 99.99%, Sinopharm) were used as the liquid metal cathode. First, Na$_2$CO$_3$ and NaCl were dried at 200 °C for more than 48 hours in a vacuum oven (Model no.: DZF-6050,
Fengling, China). Second, the Al$_2$O$_3$ crucible with the 20 kg of pre-dried Na$_2$CO$_3$-NaCl mixture and 100 kg of Sn ingot was placed in a graphite crucible that was placed inside a stainless-steel (SS) reactor heated in an electric furnace. The top of the SS reactor was cooled by circulating water, and the electrodes were installed on the top flange of the stainless-steel reactor, as shown in Fig. 2b. Third, a molybdenum (Mo) wire sheathed with an Al$_2$O$_3$ tube was inserted into the bottom of Sn as the current collector. A nickel-based alloy rod was used as the anode$^{38,39}$. Fourth, the reactor was evacuated for 10 minutes and was then refilled with Ar gas (Ar, purity: 99.99%) until the internal pressure reached 1 atm, which was repeated three times. After that, Ar was continuously introduced into the reactor at a flow rate of 500 mL/min, while the internal pressure of the reactor was maintained at 1 atm. Fifth, the temperature was increased to and kept at 400 °C for 24 hours to remove residual moisture in the Na$_2$CO$_3$-NaCl. Finally, the temperature was increased to and kept at 680 °C to melt the salt mixture, and then electrolysis was performed between the Ni-based alloy anode and the liquid Sn cathode under a constant current of 350 mA·cm$^{-2}$ supplied by a computer-controlled DC power source (Model no.: CT-8000, Neware, China). The current efficiency was measured using the measured amount of Na in the liquid Sn electrode that was divided by the theoretical amount of Na calculated from the consumed electricity by Faraday Law.
Fig. 2 Experimental apparatus for the electrolysis of molten Na$_2$CO$_3$-NaCl: a. device schematic diagram, b. optical photograph of the 100 kg-scale electrolyzer.

2.2. Preparation of liquid M-Sn alloys by displacement reactions in molten NaCl-MCl$_n$

The displacement reaction was performed in a graphite crucible heated in a tube furnace housed in an Ar-filled glovebox. All salts were dried for 48 hours at 200 °C in a vacuum oven before being transferred into the glovebox. First, the salts containing MCl$_n$ (Anhydrous, 99.9%, Aladdin, M = Li, Mg, Ca, Sr, and Ba, n = 1 or 2) were kept at 400 °C for 24 hours to remove all residual moisture. Then, the salt was melted by increasing the temperature to a target operating temperature. Second, the Na-Sn alloy was immersed in the molten salt to dictate the displacement reaction. Here, Na$_{10}$Sn (Na content is 10 at.%) and Na$_{20}$Sn (Na content is 20 at.%) that were prepared by induction-
melting Na (Ingot, 99.9%, Aladdin) and Sn (Particles, 99.99%, Aladdin) were employed to perform the displacement reaction. Third, the furnace was cooled down to room temperature after a certain period of reaction between liquid Na-Sn and molten salt. Finally, the obtained metal was separated from the solidified molten salt by breaking the crucible. The compositions of molten salt for preparing Li-Sn, Mg-Sn, Ca-Sn, Sr-Sn, and Ba-Sn were NaCl-LiCl, NaCl-MgCl₂, NaCl-CaCl₂, NaCl-SrCl₂, and NaCl-BaCl₂, respectively. The specific experimental conditions and salt compositions are shown in Table 1. The displacement efficiency was measured using the amount of M in the M-Sn alloy divided by the amount of M completely replaced by Na-Sn.

Table 1.

The experimental conditions for the displacement of Na-Sn alloy in different molten salts.

<table>
<thead>
<tr>
<th>Experiment no.</th>
<th>Molten salt composition</th>
<th>Temperature/ °C</th>
<th>Displacement time/ minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disp.1</td>
<td>NaCl-73at.%LiCl</td>
<td>650</td>
<td>180</td>
</tr>
<tr>
<td>Disp.2</td>
<td>NaCl-43at.%MgCl₂</td>
<td>550</td>
<td>180</td>
</tr>
<tr>
<td>Disp.3</td>
<td>NaCl-53at.%CaCl₂</td>
<td>600</td>
<td>180</td>
</tr>
<tr>
<td>Disp.4</td>
<td>NaCl-52at.%SrCl₂</td>
<td>650</td>
<td>180</td>
</tr>
<tr>
<td>Disp.5</td>
<td>NaCl-40at.%BaCl₂</td>
<td>750</td>
<td>180</td>
</tr>
</tbody>
</table>

Notice: The mixed salts all used eutectic components.

2.3. Preparation of M from M-Sn alloys by vacuum distillation

Elementary metals (Li, Mg, Ca, Sr, and Ba) were prepared by the vacuum distillation of their corresponding M-Sn alloys obtained by displacement reactions.
Fig. 3 shows the schematic and photographs of the vacuum distillation device, quartz distillation tower, and the SS liner. First, the Al$_2$O$_3$ crucible contained Mg-Sn alloy was placed at the bottom of a 316 SS liner in the distillation tower and the open end of the reactor was sealed by petroleum jelly and high-temperature resin. Second, the quartz distillation tower was evacuated using a mechanical pump (Model no.: RV12, Edwards, Britain), and the gas pressure in the distillation tower was measured with a vacuum gauge (Model no.: VMV-1, Navtek, China). The quartz distillation tower was placed in the resistance furnace (Model no.: JSDZ-900, Wuhan Dianlu, China), and the temperature was increased to 1100 °C and kept for 3 hours. After distillation, the distillation tower was cooled down to room temperature within the furnace. Finally, the distillation tower was filled with high-purity Ar to 1 atm and transferred to the glove box to collect Mg metal. Moreover, the specific experimental conditions of pure Sn metal, Li-Sn, Mg-Sn, Ca-Sn, Sr-Sn, and Ba-Sn alloys are shown in Table 2. The recovery rate was measured using the amount of collected $M$ divided by the amount of $M$ in the $M$-Sn alloy.
Fig. 3 Experimental apparatus for vacuum distillation: a. Device schematic diagram of the vacuum distillation, and the optical photographs of b. a quartz distillation tower and c. a 316 SS liner.

Table 2.

The experimental conditions for vacuum distillation of pure Sn and M-Sn alloys (M = Li, Mg, Ca, Sr, and Ba).

<table>
<thead>
<tr>
<th>Experiment no.</th>
<th>Alloy composition</th>
<th>Temperature/°C</th>
<th>Pressure/Pa</th>
<th>Distillation time/minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vac.1</td>
<td>Li_{20}Sn</td>
<td>900</td>
<td>5</td>
<td>90</td>
</tr>
<tr>
<td>Vac.2</td>
<td>Mg_{10}Sn</td>
<td>1100</td>
<td>10^2</td>
<td>180</td>
</tr>
<tr>
<td>Vac.3</td>
<td>Ca_{10}Sn</td>
<td>950</td>
<td>5</td>
<td>90</td>
</tr>
<tr>
<td>Vac.4</td>
<td>Sr_{10}Sn</td>
<td>950</td>
<td>5</td>
<td>120</td>
</tr>
<tr>
<td>Vac.5</td>
<td>Ba_{10}Sn</td>
<td>900</td>
<td>0.5</td>
<td>180</td>
</tr>
<tr>
<td>Vac.6</td>
<td>Pure Sn</td>
<td>1100</td>
<td>10^2</td>
<td>180</td>
</tr>
</tbody>
</table>
2.4. Characterizations

The morphologies and microstructures of the electrolytic Na-Sn alloys, displaced M-Sn alloys, and distilled M and Sn metals were characterized by scanning electron microscopy (SEM: Tescan mira3, Zeiss) equipped with an energy dispersive X-ray spectroscopy (EDS: Oxford X-MAX, Oxford). The concentration of Cl\textsubscript{2} in the exhaust gas was measured by methyl orange spectrophotometry (MO-SP: UV-1300, Macy). Additionally, the concentration of elements in the metal samples was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES: Optima 8300, PerkinElmer) or flame atomic absorption spectroscopy (FAAS: A3F, Persee).

3. Results and discussion

3.1. Preparation of liquid Na-Sn alloy

The EDD approach employs low-cost Na\textsubscript{2}CO\textsubscript{3}, NaCl, Sn, and MCl\textsubscript{n} (M = Li, Mg, Ca, Sr, Ba, n = 1 or 2) to produce M metals without Cl\textsubscript{2} emission, in which process Sn serves as a metal carrier and is not consumed (Fig.1a). The addition of Na\textsubscript{2}CO\textsubscript{3} into NaCl decreases the melting point of the electrolyte and provides CO\textsubscript{3}\textsuperscript{2-} (O\textsuperscript{2-}) that can be discharged at a more negative potential than that of Cl\textsuperscript{-}. Note that the introduction of CO\textsubscript{3}\textsuperscript{2-} does not cause carbon deposition in sodium (potassium) systems (the melt only contains Na or K cation), which significantly differs from the Li- and AEM-based molten salt systems (Fig. 4). In other words, the CO\textsubscript{3}\textsuperscript{2-}-containing sodium (potassium) molten salt is a special system that can allow the deposition of Na (K) prior to the carbon
deposition. Thus, the addition Na$_2$CO$_3$ (K$_2$CO$_3$) not only prevents the evolution of Cl$_2$ but also avoids carbon deposition. In addition, Na (K) can be deposited at the liquid Sn electrode, which prevents liquid Na (K) floating and suppresses the dissolution of Na (K) in molten salt. Therefore, the molten Na$_2$CO$_3$-NaCl (K$_2$CO$_3$-KCl) is a thermodynamically favorable system to produce Na-Sn alloys without generating Cl$_2$.

**Fig. 4.** Thermodynamic potential profiles of s-block metals and carbon deposition as a function of temperature.

However, the boiling point of K (759 °C) is close to the working temperature during the electrolysis of molten K$_2$CO$_3$-KCl (700 °C), which makes the current
efficiency of the electrolytic K-Sn alloy at a lower value. Therefore, the molten Na$_2$CO$_3$-NaCl was selected as the electrolyte in this work in order to obtain a high current efficiency. The 100 kg-scaled electrolyzer used in this work is shown in Fig. 2b, and the current efficiency of ~104.8 kg Na$_{20}$Sn alloy (Na content is 20 at.%) prepared by Na$_2$CO$_3$-NaCl electrolysis was 81.0% (Its actual composition was Na$_{16.8}$Sn, Fig. 5). And the ICP results showed that the concentrations of impurity elements in Na-Sn alloy were less than 20 ppm (Table 3). In addition, the concentration of Cl$_2$ in the exhaust gas at the different time was 0.19 mg/m$^3$, 0.16 mg/m$^3$, and 0.21 mg/m$^3$ respectively (Table 4), which are lower than the workshop air hygiene standards of China (1 mg/m$^3$, GB 11984-89). Thus, the Cl$_2$ concentration is far less than the air hygiene standards, meaning that the exhaust gas of the Na$_2$CO$_3$-NaCl electrolysis can be directly released without worrying about the harmfulness of Cl$_2$ gas. As a matter of fact, the Na-Sn electrolyzer resembled the Hall–Héroult cell, which could be potentially employed for the production of s-block metals after 150 years from the birth of the Al electrolyzer.

Fig. 5 Optical photograph of Na$_{20}$Sn alloy ingots prepared by the 100 kg-scale
electrolyzer using molten Na₂CO₃-NaCl. Its composition was determined as Na₁₆.₈₄Sn by ICP-OES.

**Table 3.**

Impurity contents of Na-Sn alloy obtained by Na₂CO₃-NaCl electrolysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ni (PPM)</th>
<th>Al (PPM)</th>
<th>W (PPM)</th>
<th>Mo (PPM)</th>
<th>Cr (PPM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 kg Na-Sn</td>
<td>13.95</td>
<td>19.60</td>
<td>3.44</td>
<td>4.10</td>
<td>4.99</td>
</tr>
</tbody>
</table>

Notice: The content of elements in samples was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) and FAAS.

**Table 4.**

The concentration of chlorine in the exhaust gas.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
<th>Unit</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas1</td>
<td>Electrolysis for 1 h</td>
<td>mg/m³</td>
<td>0.19</td>
</tr>
<tr>
<td>Gas2</td>
<td>Electrolysis for 2 h</td>
<td>mg/m³</td>
<td>0.16</td>
</tr>
<tr>
<td>Gas3</td>
<td>Electrolysis for 3 h</td>
<td>mg/m³</td>
<td>0.21</td>
</tr>
<tr>
<td>Gas4</td>
<td>Air (as a blank control)</td>
<td>mg/m³</td>
<td>Not detected</td>
</tr>
</tbody>
</table>

Notice: The detection limit for a 30 L gas sample is 0.03 mg/m³.

### 3.2. Preparation of liquid M-Sn alloys

The electrolytic Na-Sn alloy can displace Li, Mg, Ca, Sr and Ba from the MClₙ salt (M = Li, Mg, Ca, Sr, and Ba, n = 1 or 2) because of the different chemical potential of Na in liquid Sn from that of the M in liquid Sn (Fig. 6a). Thermodynamically, pure Na metal cannot displace Li, Ca, Sr, and Ba from MClₙ salt (except Mg) spontaneously (Fig. 6b). This means that the liquid Sn electrode results in the spontaneous reaction between the Na-Sn alloy and MClₙ salt. In other words, the chemical potential of M in
liquid Sn can be expressed in terms of the activity of M in liquid Sn\textsuperscript{40-43}. In this regard, the Na activity in liquid Sn is higher than that of M in liquid Sn when the concentration of Na and M are the same. Moreover, the Na-Sn alloy is inert to the oxides of M (Fig. 6c), meaning that the inclusion of a small amount of oxide will not decrease the efficiency of the displacement reactions. And the reaction of the displacement can be expressed as follow:

$$\text{Na(Sn)} + \text{MCl}_n \rightarrow \text{M(Sn)} + n\text{NaCl}$$

(1)

**Fig. 6 a.** Equilibrium potential profiles of typical redox couples at an inert electrode and the liquid Sn electrode, data from the literature\textsuperscript{7,43}. Gibbs free energy change-temperature curve for the reaction of **b.** chlorine and **c.** oxygen with s-block metal.

The 100 g of homogeneous Na\textsubscript{20}Sn alloy was melted from pure metals of Na and Sn (Fig. 7a), which was then immersed in MCl\textsubscript{n}-NaCl molten salt to perform the displacement reaction for 3 hours. As shown in Fig. 7b-f, Li\textsubscript{20}Sn, Mg\textsubscript{10}Sn, Ca\textsubscript{10}Sn, Sr\textsubscript{10}Sn, and Ba\textsubscript{10}Sn alloys were obtained after the displacement reactions between liquid Na\textsubscript{20}Sn alloy and MCl\textsubscript{n}-NaCl salts. Besides the characteristic peak of Li element in Li\textsubscript{20}Sn alloy that cannot be detected by EDS analysis, the characteristic peaks of Mg, Ca, Sr, and Ba elements were obviously observed in the EDS surface analysis of cross sections for Mg\textsubscript{10}Sn, Ca\textsubscript{10}Sn, Sr\textsubscript{10}Sn, and Ba\textsubscript{10}Sn alloys. The characteristic peak of Na
element was disappeared in the EDS pattern of M-Sn alloy. Finally, the compositions of M-Sn alloys were determined after crushing (as shown in Table 5), and the displacement efficiencies were calculated that 99.52% for Li_{20}Sn alloy, 98.44% for Mg_{10}Sn alloy, 97.97% for Ca_{10}Sn alloy, 96.60% for Sr_{10}Sn alloy, and 96.34% for Ba_{10}Sn alloy. The slightly different displacement efficiency of different M-Sn alloys is due to the different solubility of different M metals in the corresponding molten salts.

Fig. 7 Optical photographs (left), EDS (right) and SEM (inset) surface analyses of the 
a. Na_{20}Sn alloy prepared by induction melting, b. Li_{20}Sn, c. Mg_{10}Sn, d. Ca_{10}Sn, e. Sr_{10}Sn, and f. Ba_{10}Sn alloys after displacement reactions.

Table 5.

The results of Na-Sn alloy displacement in different molten salts.
<table>
<thead>
<tr>
<th>Disp.</th>
<th>Alloy</th>
<th>Na content</th>
<th>Sn content</th>
<th>Vapor Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Na₁₀Sn</td>
<td>Li₉.₈₅₆Na₀.₀₀₅Sn</td>
<td>99.₄₅</td>
<td></td>
</tr>
<tr>
<td>NaCl-LiCl</td>
<td>Na₂₀Sn</td>
<td>Li₁₉.₇₈₄Na₀.₀₀₅Sn</td>
<td>99.₅₂</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Na₁₀Sn</td>
<td>Mg₄.₈₆₅Na₀.₀₀₂Sn</td>
<td>9₈.₁₈</td>
<td></td>
</tr>
<tr>
<td>NaCl-MgCl₂</td>
<td>Na₂₀Sn</td>
<td>Mg₉.₇₈₅Na₀.₀₀₃Sn</td>
<td>₉₈.₄₄</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Na₁₀Sn</td>
<td>Ca₄.₇₆₁Na₀.₀₀₄Sn</td>
<td>₉₆.₀₈</td>
<td></td>
</tr>
<tr>
<td>NaCl-CaCl₂</td>
<td>Na₂₀Sn</td>
<td>Ca₉.₇₃₈Na₀.₀₀₅Sn</td>
<td>₉₇.₉₇</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Na₁₀Sn</td>
<td>Sr₄.₇₆₃Na₀.₀₀₁Sn</td>
<td>₉₆.₁₃</td>
<td></td>
</tr>
<tr>
<td>NaCl-SrCl₂</td>
<td>Na₂₀Sn</td>
<td>Sr₉.₆₆₂Na₀.₀₁₀Sn</td>
<td>₉₆.₆₀</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Na₁₀Sn</td>
<td>Ba₄.₇₅₇Na₀.₀₀₉Sn</td>
<td>₉₆.₀₀</td>
<td></td>
</tr>
<tr>
<td>NaCl-BaCl₂</td>
<td>Na₂₀Sn</td>
<td>Ba₉.₅₇₆Na₀.₀₁₃Sn</td>
<td>₉₆.₃₄</td>
<td></td>
</tr>
</tbody>
</table>

Notice:

1. The content of elements in the alloy was determined by ICP-OES and FAAS.
2. The Na content in the melted Na₁₀Sn alloy was 9.₉₁ at.%.
3. The Na content in the melted Na₂₀Sn alloy was ₁₉.₈₈ at.%.

3.3. Separation of M-Sn alloys

The saturated vapor pressure versus temperature for Li, Na, Mg, Ca, Sr, Ba and Sn metals is shown in Fig. 8a, which is calculated by the Antoine equation,

\[ \log p = \frac{A}{T} + B \log T + CT + D \]  

3-1

where \( p \) is the saturated vapor pressure (in mmHg), \( T \) is the temperature (in K), and \( A, B, C, \) and \( D \) are the constant coefficients (shown in Table 6). Since the vapor pressure of M metals (M = Li, Mg, Ca, Sr, and Ba) is several orders of magnitude higher than that of Sn metal, M metals can be separated by vacuum distillation from displaced M-Sn alloys.

Table 6.
Constant coefficients of metal vapor pressure formula.

<table>
<thead>
<tr>
<th>Metal</th>
<th>A</th>
<th>B</th>
<th>$C \times 10^3$</th>
<th>D</th>
<th>Temperature range / K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>-8415</td>
<td>-1</td>
<td>—</td>
<td>11.34</td>
<td>454 ~ 1613</td>
</tr>
<tr>
<td>Na</td>
<td>-5780</td>
<td>-1.18</td>
<td>—</td>
<td>11.50</td>
<td>298 ~ 1156</td>
</tr>
<tr>
<td>Mg</td>
<td>-7550</td>
<td>-1.41</td>
<td>—</td>
<td>12.79</td>
<td>922 ~ 1380</td>
</tr>
<tr>
<td>Ca</td>
<td>-8920</td>
<td>-1.39</td>
<td>—</td>
<td>12.45</td>
<td>1112 ~ 1757</td>
</tr>
<tr>
<td>Sr</td>
<td>-18803</td>
<td>—</td>
<td>—</td>
<td>16.056</td>
<td>1213 ~ 1413</td>
</tr>
<tr>
<td>Ba</td>
<td>-9340</td>
<td>—</td>
<td>—</td>
<td>7.42</td>
<td>998 ~ 1873</td>
</tr>
<tr>
<td>Sn</td>
<td>-17131</td>
<td>—</td>
<td>—</td>
<td>9.64</td>
<td>505 ~ 2543</td>
</tr>
</tbody>
</table>


The Mg$_{10}$Sn alloy prepared by displacement was converted to Mg and Sn metals through vacuum distillation. As shown in Fig. 8b, the pressure started to increase from 970 °C, at which temperature the Mg metal started to evaporate from Mg$_{10}$Sn alloy, leading to the separation of Mg and Sn metals. For comparison, no peak was observed from the pure Sn. At 970 °C, the pressure increased from 100 Pa to 120 Pa and then decreased to 100 Pa, meaning that it only took 75 minutes to complete the vaporization separation. After vaporization, the deposited Mg metal was observed on the inside wall of the 316 SS liner (Fig. 8c$_1$). Since Na is so reactive, the sublimate became sodium oxide (Fig. 2k, right) when exposed to the air. Since Mg metal was collected in a glove box, there was no characteristic peak of oxygen element appeared in the EDS pattern (Fig. 8c$_2$). After vacuum distillation, the Mg$_{10}$Sn alloy became pure Sn (Fig. d) at the bottom of the distillation tower. The recovery rate of Mg metal is 91.7%, which can be further increased by improving the equipment.
**Fig. 8 a.** Vapor pressure-temperature profiles of Li, Na, Mg, Ca, Sr, Ba and Sn metals.

**b.** Variation in temperature and gas pressure during the vacuum distillation of Mg-Sn alloy. **c.** Optical photograph (c₁), EDS (c₂) and SEM (inset c₂) surface analyses of the sediment on the 316 stainless-steel liner wall after vacuum distillation. **d.** Optical photograph (d₁), EDS (d₂) and SEM (inset d₂) surface analyses of the residue at the bottom of the distillation tower after vacuum distillation.

Li metal was obtained by vacuum distillation from displaced Li₂₀Sn alloy. During vacuum distillation, the pressure suddenly changed at 1005 °C, increased from 130 Pa to 170 Pa and then decreased to 130 Pa, indicating that Li metal was vaporized and separated from the Li-Sn alloy at this time and the separation process lasted for 120 minutes (Fig. 9a). After vaporization, the deposited Li metal was observed at the inside wall of the 316 SS liner (Fig. 9b). Li metal was collected after cutting the 316 SS liner in the glove box and the recovery rate of Li metal is 90.5% at the lab scale.
Fig. 9 a. Variation in temperature and gas pressure during the vacuum distillation of Li-Sn alloy. b. Optical photograph of the sediment on the 316 stainless-steel liner wall after vacuum distillation.

After displacement reactions, Li, Mg, Ca, Sr and Ba were vacuum-distilled from the M-Sn alloys. The separation rates were 99.4% for Li, 96.3% for Mg, 93.8% for Ca, 95.1% for Sr, and 95.5% for Ba (Table 7). After distillation, Sn metal was recycled with a recovery efficiency of >99.9%. Note that the residual M metal remained in Sn metal can be recycled in the following displacement process. Hence, we can prepare Cl₂-free Li, Mg, Ca, Sr, and Ba metals using the Na-Sn alloy mediator that can be prepared in molten Na₂CO₃-NaCl. The green Li, Mg, Ca, Sr, and Ba metals are promising feedstock for preparing next-generation metal-electrode batteries.

Table 7.

The results of M-Sn alloys after vacuum distillation (M = Li, Mg, Ca, Sr, and Ba).

<table>
<thead>
<tr>
<th>Experiment no.</th>
<th>Sediment composition</th>
<th>Residue composition</th>
<th>Separation rate/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vac.1</td>
<td>Na₀.₀₂₃Li</td>
<td>Li₀.₁₁Sn</td>
<td>99.4</td>
</tr>
<tr>
<td>Vac.2</td>
<td>Na₀.₀₃₆Mg</td>
<td>Mg₀.₃₈Sn</td>
<td>96.3</td>
</tr>
<tr>
<td>Vac.3</td>
<td>Na₀.₀₈Ca</td>
<td>Ca₀.₆₆Sn</td>
<td>93.8</td>
</tr>
<tr>
<td>Vac.4</td>
<td>Na₀.₁₅Sr</td>
<td>Sr₀.₄₇Sn</td>
<td>95.1</td>
</tr>
</tbody>
</table>
Notice:

1. The content of elements in the alloy was determined by ICP-OES and FAAS.

2. Na$_{0.023}$Li is Na-Li alloy with Na content of 0.023 at.%.

**Conclusions**

We developed a clean and efficient electrolysis-displacement-distillation (EDD) approach to preparing pure Li, Mg, Ca, Sr, and Ba metals without generating Cl$_2$. Thanks to the thermodynamic properties of Na$_2$CO$_3$ and Na-Sn alloy, the electrolysis of molten Na$_2$CO$_3$-NaCl precluded generating carbon, pure Na and Cl$_2$ in the electrolyzer. The current efficiency of the 100 kg-scaled Na-Sn alloy electrolyzer under a constant current of 350 mA·cm$^{-2}$ reached 81.0%. Li-Sn, Mg-Sn, Ca-Sn, Sr-Sn, and Ba-Sn alloys were successfully displaced by Na-Sn alloys from molten NaCl-LiCl, NaCl-MgCl$_2$, NaCl-CaCl$_2$, NaCl-SrCl$_2$, and NaCl-BaCl$_2$ with a displacement efficiency of >96.0%. Finally, Li, Mg, Ca, Sr, and Ba metals were successfully separated from M-Sn alloys using the vacuum distillation with a separation rate of >95.0%. More broadly, this technology can also be used to prepare various reactive metals such as transition metals and rare earth metals, offering clean materials for next-generation energy-storage devices and engineering applications.

**Author Contributions**

Lei Guo and Huayi Yin conceived the idea, Dihua Wang and Huayi Yin supervised the project, Lei Guo, Huayi Yin and Dihua Wang designed the experiment, Lei Guo
conducted experiments and analyzed the data, Zuojun Hu, Yongxin Wu, Shuaibo Gao and Fangzhao Pang assisted with displacement and distillation experiments, Lei Guo prepared the manuscript, all authors discussed the results of this work, Dihua Wang and Huayi Yin edited the manuscript, and Huayi Yin submitted this work.

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