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Non-contact gaseous microplasma electrode as anode for electrodeposition of metal and metal alloy in molten salt

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ABSTRACT

Microplasma based on glow discharge could act as a non-contact gaseous electrode and has attracted much attention in both fundamental research and application. Herein, with microplasma as the anode, the electrodeposition process of a series of metal and metal alloys in molten salt has been systemically studied. Four metal cations with different valence states, silver (Ag^+), nickel (Ni^{2+}), copper (Cu^{2+}), and iron (Fe^{3+}), could all be reduced on the solid cathode with high current efficiency and the corresponding metal products were of high purity. The electrodeposition of aluminum-lanthanum (Al-Ln) alloy on the aluminum cathode was also successfully carried out with microplasma as the anode, and the same alloy was obtained by using the conventional anode electrode. These results indicated that microplasma anode based on non-contact direct-current (DC) glow discharge is a promising electrode to be applied in molten salt electrolysis.

Molten salt electrolysis has high efficiency and selectivity. It has been developed as a common method for depositing metals or synthesizing functional materials in recent years [1,2]. Compared with the aqueous solution, molten salt has a wider electrochemical window and higher conductivity, and is often used in metal metallurgy, the rare earth chemical industry, and spent fuel reprocessing [3–7]. However, the high temperature of hundreds or even a thousand degrees Celsius in the electrolysis process will lead to more serious problems such as the corrosion of solid anode, which puts forward more strict requirements for the selection of anode materials. In this case, graphite rod and precious metal platinum seem to be the optimal materials for the anode in most molten salt systems, but for some special systems, such as metal oxide reduction in LiCl-Li_2O and $CaCl_2$-CaO, graphite rod and metal platinum will also face many problems [8–13].

In recent years, microplasma has been applied as a new gaseous electrode in the field of electrolytic research [14,15]. Since there is no solid electrode in contact with the electrolyte, the charge transfer between the electrode and the electrolyte will be carried out by gas-phase electrons or ions in the plasma [16–18]. Due to the absence of the traditional solid-liquid contact interface, the electrochemical reaction under the excitation of the microplasma electrode is different from the traditional reaction and the microplasma might serve as an alternative new electrode for the anode in molten salt electrolysis. But sadly, the research of plasma in molten salt electrolysis has been poorly studied in the last decades. The utilization of low-pressure glow discharge to prepare dendritic metals through cathode discharge electrolysis of molten salts by Brenner and Sligh [19] seems to be the first plasma research applied to molten salt. Subsequently, the Ito research group in Japan also carried out some studies on the application of plasma in molten salt, and successfully obtained a series of metal and alloy nanoparticles in molten salt by inducing the cathode with the plasma of atmospheric-pressure arc discharge [20–27]. However, in arc discharge mode, if the plasma is used as the anode, the positive ions would be introduced into the electrolyte through the oxidation of the metal anode, resulting in a large amount of anode consumption.

In our previous work, it was found that microplasma based on atmospheric-pressure glow discharge can effectively avoid anode corrosion and will not introduce contaminated ions, making it promising to become a substitute for the traditional platinum elec-

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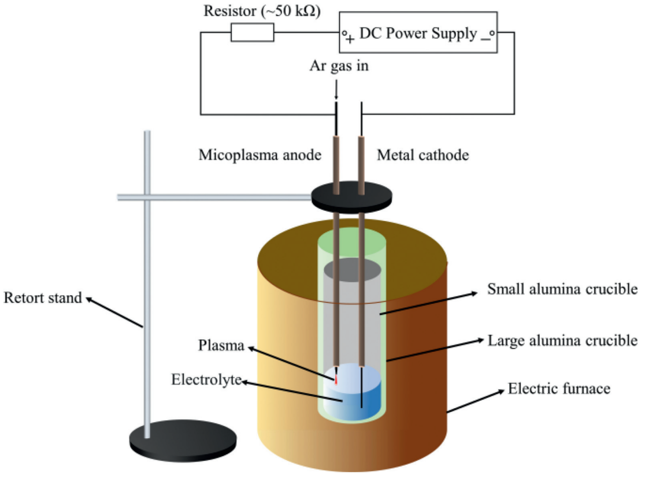

Fig. 1. Schematic of experimental apparatus for microplasma anode-discharge electrolysis in molten salt.

trode and graphite carbon rod [28]. The plasma excited in the electrolysis process can also be used as the excitation source of atomic emission spectroscopy (AES) for *in situ* analysis and real-time monitoring of the ion concentration through the spectrum, showing its promising application in molten salt electrolysis [29]. While, the study on microplasma anode in molten salt is still rare, it is highly needed to investigate its behavior in different electrochemical reactions for better understanding and application.

In this work, to fill the blank in the application of glow discharge microplasma anode in molten salt electrolysis and investigate the mechanism, the electrodeposition process of a series of metal and metal alloys in molten salt with the microplasma as the anode was systemically studied. Four metal cations with different valence states, Ag^+, Ni^{2+}, Cu^{2+}, and Fe^{3+}, were reduced on the solid cathode with the microplasma as the anode and the corresponding metal products were of high purity. Metal aluminum is widely used in extracting the lanthanide and actinide ions from molten salt [5,6,30-32] in the rare earth industry and spent fuel reprocessing. To verify the feasibility of microplasma anode in these areas, the electrodeposition of Al-Ln alloy on the aluminum cathode with microplasma as the anode was also carried out.

Firstly, the feasibility of the electroreduction of different valence metals with microplasma anodes in molten salt electrolysis was studied. A gravimetric method widely used in electrodeposition research has been applied to quantify the metal cations reduction on the solid cathode, by studying the electrodeposition products and estimating faradaic efficiency. The experimental setup for microplasma-induced anode discharge electrolysis is shown in Fig. 1. With flowing argon gas through a hollow stainless-steel capillary tube (diameter ~1.6 mm), the plasma was ignited by applying a DC voltage of ~2 kV, and fixed approximately 2 mm away from the molten salt surface. Molybdenum wire was used as a solid cathode. As mentioned previously, the charge will be transported through the plasma generated between the interface of the plasma anode and the molten salt and participate in the electrochemical reaction in the molten salt. According to the law of redox reaction, metal cations will be reduced to metal at the solid cathode, and chlorine gas will be generated at the plasma-molten salt interface:

$$\text{Anode: } 2Cl^- - 2e^- = Cl_2 \uparrow \quad (1)$$

$$\text{Cathode: } M^{z+} + ze^- = M \downarrow \quad (2)$$

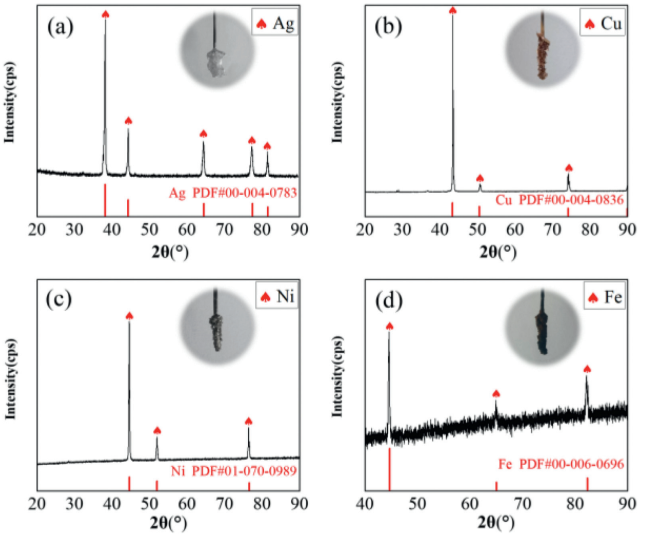

Fig. 2. XRD analysis and macroscopic morphology of the products obtained from the microplasma-induced anode discharge electrolysis under 773 K, 20 mA galvanostatic electrolysis for 1 h: (a) LiCl-KCl-AgCl; (b) LiCl-KCl-$CuCl_2$; (c) LiCl-KCl-$NiCl_2$; (d) LiCl-KCl-$FeCl_3$.

Four different metal cations: Ag^+, Ni^{2+}, Cu^{2+}, and Fe^{3+} were selected as the research objects and introduced into the molten salt electrolyte by adding corresponding metal chlorides. To avoid the influence of other factors, the chlorides added during this experiment were all 2.0 mmol, the proportion and the mass of molten salt electrolyte were also kept unchanged (LiCl: 12.7 g, KCl: 14.9 g) to ensure the same concentration of metal cations in the four groups of experiments. The experimental temperature was controlled at 773 K. The plasma was ignited and ran for 1 h under a constant current of 20 mA. After electrolysis, the cathode was removed from the molten salt and the product was characterized after treatment. The corresponding X-ray diffraction (XRD) patterns and images of products obtained in the four groups of experiments were shown in Fig. 2, and the microscopic morphologies and element distribution characterized by scanning electron microscope (SEM) and energy dispersive spectrometer (EDS) were shown in Fig. 3 separately. The results showed that at the bottom of the solid cathode, the four groups of electrolysis experiments had obtained obvious metallic deposits with different morphologies and colors. The peaks on the XRD of the sediments were identical to the standard PDF cards that correspond to metals reduced by metal cations in the molten salts, and there were nearly no impurity peaks, which confirmed the reduction of metals at the cathode. These results suggested that no matter the simple univalent metal ion Ag^+, divalent ions Ni^{2+}, and Cu^{2+} or trivalent variable metal ion Fe^{3+}, they could all be reduced in molten salt with the microplasma as the anode and the corresponding metal products with high purity on the solid cathode were obtained, which verified the feasibility of the microplasma anode in molten salt electrolysis. The microstructure analyzed by SEM and EDS further confirmed the composition of the samples and showed that the four metal cations were deposited in the form of dendrites at the cathode, which was similar to traditional electrolysis.

To quantify the reduction of different valence metal cations, the weight of the reduced metal was measured and compared to the theoretical amount based on the total charge passed. The ratio of the measured mass to the predicted mass was defined as the Faradaic efficiency [14,33]. The theoretical mass m_f was calculated using Faraday's law of electrolysis.

$$m_f = ItM/zF \quad (3)$$

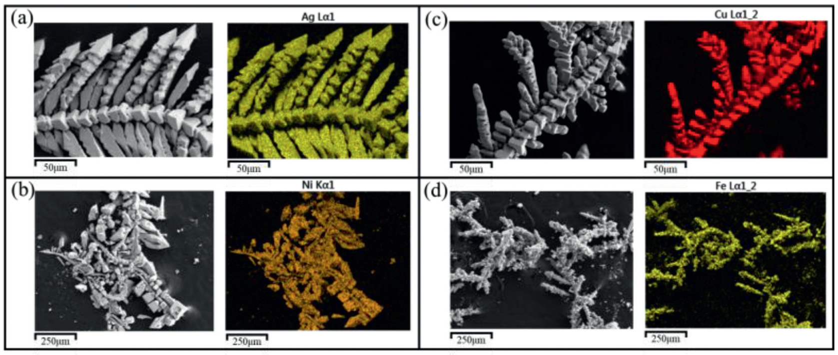

Fig. 3. SEM with EDS analysis of the metal obtained by microplasma-induced anode discharge electrolysis under 773 K, 20 mA galvanostatic electrolysis for 1 h: (a) LiCl-KCl-AgCl; (b) LiCl-KCl-$CuCl_2$; (c) LiCl-KCl-$NiCl_2$; (d) LiCl-KCl-$FeCl_3$.

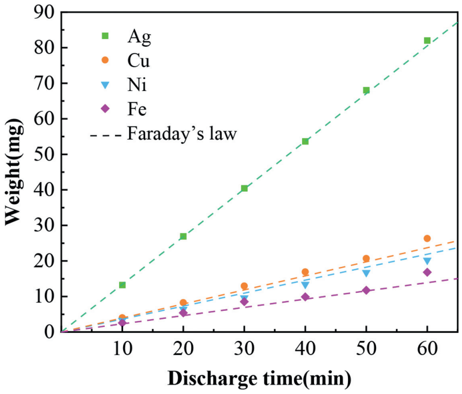

Fig. 4. Weight measured for collected Ag, Cu, Ni, and Fe after operating a microplasma anode at various times. The various metal weight predicted by Faraday's law is also shown (dashed line).

where I is the current of electrolysis, t is the electrolytic time, F is Faraday's constant, z is the number of electrons transferred in the reaction ($z = 1$ for Ag^+, 2 for Ni^{2+} and Cu^{2+}, 3 for Fe^{3+}), and M is the molar mass constant of metal. The Faradaic efficiency (FE) was then defined as the ratio of m and m_f.

$$FE = m/m_f \tag{4}$$

where m is the mass of metal obtained by weighing the products generated at the cathode.

Fig. 4 showed the measured weight of metal collected at the molybdenum cathode for various microplasma anode discharge times and Table S1 (Supporting information) summarized all the results of Faraday efficiency varying with electrolysis time. It is evident that the mass of the four metals deposited on the cathode was proportional to the discharge time, and all of them increased with the discharge time, which fully accorded with Faraday's law.

Within 1 h of electrolysis of univalent metal ion Ag^+, Faraday efficiency was close to 100%, indicating that for the electric reduction of the simple valence state univalent Ag^+, the actual charge through the whole circuit was close to the theoretical value. In the case of no solid-liquid contact at the anode, the plasma perfectly undertakes the task of charge transfer in the circuit. When the electrolysis time was extended to 2 h, the Faraday efficiency decreased significantly, which was mainly caused by the decrease of Ag^+ concentration. Since the total amount of Ag^+ added to the electrolyte was only 2.0 mmol (under the 20 mA current, the electrolytic process would complete within 2.68 h theoretically). Without the introduction of additional metal sources, the electrolytic process for 2 h would consume about 74.6% of Ag^+, and lead to the continuous reduction of the limiting current on the cathode surface. Therefore, when the limiting current of Ag^+ was reduced to less than 20 mA, the excess current would no longer participate in the reduction of Ag^+, which was reflected in the decline of Faraday efficiency.

The Faraday efficiency of bivalent metal ion Cu^{2+} and trivalent metal ion Fe^{3+} was slightly more than 100%, and the Faraday efficiency of metal Fe was higher than that of metal Cu. The main reason for this phenomenon was that metal Cu and Fe were easily oxidized in air and water, though the reduction process was completed in the glove box without water and oxygen, the oxidation of some products was inevitable during the subsequent cleaning and drying process. Since the relative atomic mass of Cu and Fe was small, the relative molecular mass of the oxide and the relative atomic mass ratio of the metal were 1.5 and 1.86, respectively, the mass of the oxidized part could not be ignored, which had a great impact on the overall Faraday efficiency. Therefore, the Faraday efficiency of Cu and Fe was higher than 100%, and metal Fe was higher than metal Cu. Since the oxidation of metals Fe and Cu accounts for a small proportion in the product (no obvious characteristic peak of oxides was detected in the XRD results), a more than 100% Faraday efficiency still indicated that the microplasma anode had good electrolytic efficiency and selectivity in reduction of metal ions Cu and Fe. For the divalent metal ion Ni^{2+}, its Faraday efficiency was lower than that of other metals, but it was still more than 85%. The possible reason is there were side reactions in the reduction process of Ni^{2+}, and some electrons did not participate in the reduction of Ni^{2+}.

It is a widely researched direction in the field of molten salt electrochemistry to extract and recover actinide and lanthanide elements from spent fuel by molten salt electrolysis or to introduce rare earth elements into active metals to prepare alloys with excellent properties. In this kind of molten salt system, the reduction mechanism of actinide and lanthanide ions is slightly different from that of ordinary metal ions. Since the reduction potential of lanthanide actinides is generally more negative than Li^+ [5,7], they cannot be reduced within the electrochemical window of LiCl-KCl molten salt, so active aluminum metal is usually used as the electrodeposition cathode through the principle of underpotential deposition [34] to produce alloy. For the anode, graphite rods or expensive precious metal electrodes such as platinum are used.

To verify whether underpotential deposition also exists in the discharge process of microplasma anode, and explore the feasibility of gas electrodes replacing traditional electrodes in spent fuel reprocessing, the electrodeposition of cerium (Ce) and samarium (Sm) on the aluminum cathode was studied. 1.5 mmol of anhydrous $CeCl_3$ and $SmCl_3$ were respectively added into LiCl-KCl molten salt with fixed proportion and mass, and aluminum foils were used as the cathode. The obtained samples through the

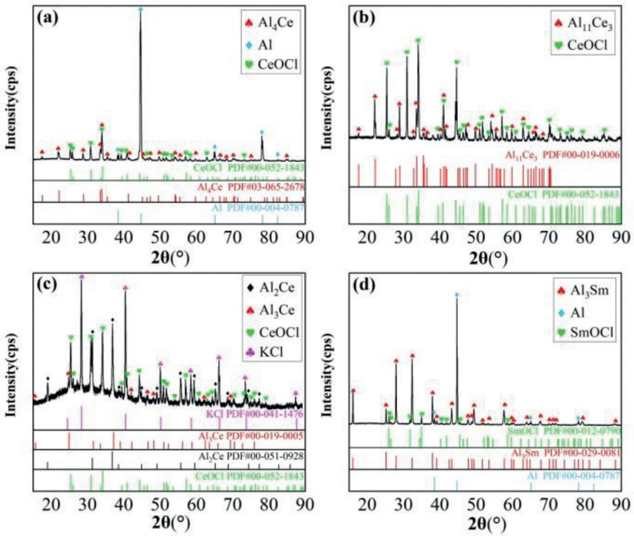

Fig. 5. XRD analysis of the aluminum foils after the microplasma-induced anode discharge electrolysis under 773 K, 20 mA galvanostatic electrolysis: in the LiCl-KCl-CeCl$_3$ (1.5 mmol) melts discharge (a) for 1 h, (b) for 2 h, (c) for 3 h; (d) in the LiCl-KCl-SmCl$_3$ (1.5 mmol) melts discharge for 2 h.

microplasma-induced anode discharge were treated and characterized after electrolysis.

The XRD results (Fig. 5) showed that Ce^{3+} and Sm^{3+} in molten salt were successfully reduced on the surface of aluminum foils by microplasma anode, and formed Al-Ce and Al-Sm alloys with metal aluminum. Metal oxychloride was a common byproduct of rare earth elements, which was generated by the reaction of anhydrous CeCl$_3$ and SmCl$_3$ at high temperatures in our samples. Since it was insoluble in molten salt and water, it would be embedded in the alloy and taken out from the molten salt with the cathode. At the same time, Ce^{3+} was taken as the research object to study the influence of different plasma electrolytic times on the alloy composition on the cathode surface. It was found that under the constant current of 20 mA, the alloy obtained by electrolysis for 1 h was Al$_4$Ce, for 2 h was Al$_{11}$Ce$_3$, and for 3 h was Al$_2$Ce and Al$_3$Ce. With the increase of electrolysis time, the Al-Ce alloy on the aluminum foil surface gradually changed into the alloy phase with more metal Ce enrichment, indicating that the reduction reaction of Ce^{3+} was gradually carried out. It was proved that Ce^{3+} was reduced and enriched on an aluminum foil surface by underpotential deposition, and it was similar to the traditional solid anode [6,35,36]. These phenomena further indicate that as a new gas electrode, the microplasma electrode also follows the general electrochemical law and is suitable for the manufacture of rare earth alloys.

In summary, the Ag^{+}, Ni^{2+}, Cu^{2+}, and Fe^{3+} ions have been successfully reduced to corresponding metals in LiCl-KCl molten salt system by using microplasma anode, thus verifying the feasibility of microplasma electrode acting as an anode in molten salt electrolysis. The Faraday efficiency of the four metals was slightly different, univalent metal ion Ag^{+} was close to 100% within electrolysis for 1 h, but with the increase of electrolysis time, its efficiency would gradually decrease. Due to oxidation, the Faraday efficiency of bivalent metal ion Cu^{2+} and trivalent metal ion Fe^{3+} was slightly more than 100%. For the divalent metal ion Ni^{2+}, its Faraday efficiency was lower than that of other metals, but it was still more than 85%. By replacing the cathode with aluminum foils, Al-Ce and Al-Sm alloys could also be obtained on the active aluminum cathode by underpotential deposition. Based on these researches, as a new gaseous electrode, the microplasma electrode followed the general electrochemical law and was suitable for the general application in the field of molten salt electrochemistry. The proof-of-concept experiments in this work have shown that the microplasma anode could offer a new choice as an anticorrosive electrode for molten salt electrolysis, due to its unique charge transfer property, and may have great significance for the whole field of electrochemistry.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2023.108483.

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