Editorial for special issue on high-temperature molten salt chemistry and technology

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High-temperature molten salt consisting of metal cation and non-metal anion is a promising media to break the limits of aqueous solution due to high conductivity, wide electrochemical window, rapid mass transfer, high solubility to reactants, low vapor pressure, etc. In the past two hundred years, high-temperature molten salt chemistry and technology attract widely interests. Particularly, molten salt electrolysis as an indispensable metallurgy technology has been applied industrially for metal extraction of Al, rare earth, and alkali/alkaline-earth metals. It is well known that industrial aluminum electrolysis was invented by Hall and Heroult in the end of the 19th century. It is a milestone and promotes the change of Al from noble metal to bulk metal. At present, the yield of Al has reached to 62 millions tons all over the world in 2019. High-temperature molten salt chemistry and technology has brought a revolutionary advancement to human life and infrastructure construction.

Since the 21st century, the application and investigation of molten salt chemistry and technology were further extended. Various novel electrolysis methods, such as FFC, OS, USTB etc., were proposed for the extraction of high melting point metals (i.e., Ti, V, Si etc.). Besides traditional metallurgy, high-temperature molten salts chemistry and technology were also used for the preparation of functional materials and the treatment of secondary resources and energy storage. High-temperature molten salt chemistry and technology have become an interdisciplinary including chemistry, physics, metallurgy, energy, environmental, and so on. It is expected to inject vitality to the development of traditional industries and will become a research hotspot.

It is our honor as Guest Editors of the journal *International Journal of Minerals, Metallurgy and Materials* to organize the special issue on the topic of “High-temperature molten salt chemistry and technology.” It includes thirteen novel research articles and three comprehensive reviews. All pa-

pers were mainly focused on advanced electrometallurgy, recovery and utilization of secondary resources, and the preparation of functional materials and rechargeable batteries in molten salts. The original works will provide insight to understand the recent development and frontiers of high-temperature molten salt chemistry and technology.

Electrometallurgy in high-temperature molten salts still receives the largest attentions. Particularly, the extraction of refractory metals and the separation of rare earth were mainly studied. FFC Cambridge Process for Ti extraction by the electrodeoxidation of solid TiO_2 cathode in CaCl_2 molten salts was proposed in December 1999. Generally, calcium titanate was considered as an inevitable intermediate. Wang *et al.* [1] used calcium titanate as solid cathode and the electrodeoxidation behavior was investigated. It was found that the reduction rate of $\text{Ca}_3\text{Ti}_2\text{O}_7$ was larger than that of CaTiO_3 due to more “diffusion channels” which was created by the release of Ca^{2+} . Meanwhile, a new method was also proposed to convert and recycle excess CaO from $\text{Ca}_3\text{Ti}_2\text{O}_7$ precursor. In addition, metal Cr was also successfully obtained by the electrodeoxidation of solid Cr_2O_3 cathode based on solid oxide membrane-assisted FFC Cambridge Process [2]. It was found that large porosity, small particle size, and high voltage can accelerate the reduction rate. The reduction of Cr_2O_3 proceeded in a two-step process, i.e. Cr_2O_3 to CrO , and then to Cr. Compared with aqueous electrolytes, high-temperature molten salts may lead to unwanted electrode-electrolyte interactions. Chen [3], one of inventors of FFC Cambridge Process, provided a profound review focusing on various interactions between molten salts and solid cathodes. Typical perovskitisation, non-wetting of molten salts on metals, carbon contamination to products, and the formation of oxychlorides and calcium intermetallic compounds were discussed in detail. The proper understanding to various interactions was crucial to develop the optimum and feasible

approaches for metal extraction.

OS process is another important molten salt electrochemical technology for Ti extraction. An upgraded OS process was proposed by Ahmadi *et al.* [4]. TiN or $\text{TiO}_x\text{C}_y\text{N}_z$ was firstly synthesized by simultaneous carbothermal reduction and nitridation of ilmenite (FeTiO_3), and then transformed to a high-purity TiS_2 by S_2 gas. Ti powders were further prepared by OS process from TiS_2 and the quality was much better than that by conventional OS process from TiO_2 .

It is well known that metal oxides or sulfides were usually insoluble and can only be electroreduced to metal in solid phase. Generally, the reduction rate and current efficiency are low. Soluble metal fluorides were beneficial to be reduced to metals with high purity. Wu *et al.* [5] prepared dendritic metal Hf in a $\text{NaCl-KCl-NaF-K}_2\text{HfF}_6$ molten salt. It was found that the reduction mechanism of Hf (IV) depended on NaF concentration. One-step reduction process can be achieved and disproportionation reaction between Hf metal and Hf complex ions can be effectively inhibited at high NaF concentrations ($17.39 < \text{molar ratio of } [\text{F}^-/\text{Hf}^{4+}] < 23.27$).

Rare earth was usually extracted by molten salt electrolysis. Sun *et al.* [6] separated Nd from Cu_6Nd alloy as anode by electrorefining in $\text{NaCl-KCl-0.5mol\%NdCl}_3$ molten salt. On Mo cathode, Nd without any Cu was electrodeposited. However, on Fe cathode, NdFe alloy with the ratio of 1:1 was obtained. On the other hand, the separation of rare earth from fission products was a key problem for the reprocessing of spent nuclear fuel. The electrodeposition of rare earth on inert and reactive cathodes was widely studied. Yin *et al.* [7] compared the electrochemical and underpotential deposition behavior of samarium (Sm) on various reactive metal electrodes (M) in LiCl-KCl molten salt. It was confirmed that Sm metal can not be electrodeposited on inert electrode, but Sm-M alloys were obtained by underpotential deposition due to the depolarization effect. The depolarization values of reactive metals were arranged in the following order: $\text{Zn} > \text{Al} > \text{Ni} > \text{Cu}$.

For both the extraction of refractory metals and the separation of rare earth by molten salt electrochemical technology, the electroreduction of metals with high valence usually proceeded by a multi-step electron-transfer process on conventional solid cathode, which will lead to large polarization degree. Liquid metal cathodes attracted wide interests due to the depolarization effect and direct preparation of alloys. Jiao *et al.* [8] discussed the properties of liquid metal cathodes and their selection rules in a comprehensive review. The development of liquid metal cathodes for molten salt electrolysis, specifically the extraction of Ti and the separation of rare earth, was summarized. An attractive and promising strategy for the preparation of liquid Ti alloys via molten oxide electrolysis on liquid metal cathodes was also reviewed.

Molten salt electrolysis was also an environmentally friendly method for the recovery and utilization of secondary

resources, such as CO_2 and metal solid wastes. Hu *et al.* [9] transformed CO_2 into S-doped carbon nano-fibers (CNFs) based on the capture of CO_2 by molten salts and subsequent electrochemical reduction. It was found that the catalysts (such as NiO , Co_2O_3 , and Fe_2O_3) and cathode materials can change the diameter distribution and morphology of CNFs. Liu *et al.* [10] provided a novel method to effectively separate Fe and Mn from simulated chlorinated vanadium slag by molten salt electrolysis. One-step electroreduction of Fe^{2+} and Mn^{2+} in the form of FeCl_2 and MnCl_2 in NaCl-KCl molten salt was confirmed. Fe was firstly recovered at low cell voltage, and then Mn at high cell voltage. Xi *et al.* [11] presented a good review about application of molten salts and progress of molten salt electrolysis in secondary metal resource recovery. The applications of molten salts in chemistry, electrochemistry, and energy and thermal storage were elaborated. The research progresses to metal recovery by molten salt electrolysis from various wastes, such as magnet scrap, nuclear waste, and cemented carbide scrap, were discussed comprehensively.

In view of the distinctive physicochemical properties, high-temperature molten salts were also good medium for the preparation of advanced materials. Tian *et al.* [12] proposed a feasible method for one-step N-doping to carbon paper by molten salt electrolysis in $\text{LiCl-KCl-Li}_3\text{N}$ molten salt. N content in carbon paper was up to 13wt%. N-doping carbon paper was expected to be a potential positive material for Al-ion battery. Fe-Ni36 Invar alloy was prepared via one-step electrolysis of mixed oxides in molten carbonates by Dou *et al.* [13]. The method may be an energy-effective and low-carbon emission strategy to prepare various Fe-based alloys. Zhou *et al.* [14] fabricated $\text{Ta}_3\text{N}_5/\text{TaOH}$ composites by pyrolysis of $\text{Ta}_2\text{O}_5/\text{melamine}$ mixture in molten chlorides. It was found that TaON nanoparticles were closed anchored to Ta_3N_5 nanorods. The composites with heterojunction exhibited an enhanced photocatalytic activity for degradation of methylene blue.

Rechargeable batteries with molten salt electrolyte may become a promising direction in future. Wang *et al.* [15] used $\text{AlCl}_3\text{-NaCl}$ inorganic molten salt as electrolyte of Al-ion battery. It was confirmed that flake graphite stacked with graphene nanosheets as positive electrode delivered a high capacity of $\sim 219 \text{ mAh} \cdot \text{g}^{-1}$ over 1200 cycles at $5 \text{ A} \cdot \text{g}^{-1}$ and the Coulombic efficiency was about 94.1%. Recently, liquid metal batteries have attracted wide attention and molten salts were indispensable electrolyte. Ning *et al.* [16] designed a $\text{Ca}[\text{LiCl-NaCl-CaCl}_2]\text{Ca-Pb}$ battery. The dissolution of Ca in electrolyte was successfully suppressed by multi-cation electrolyte and alloy electrode. High discharge voltage of 0.6 V and coulombic efficiency of 99% were obtained.

The special issue summarized some of the latest advancement in high-temperature molten salt chemistry and technology, which will provide helps for readers to explore new re-

search directions in the interdisciplinary fields of metallurgy, materials, environment, energy, and so on. So, we are appreciated to all authors for their innovative works and all reviewers for their helpful comments. We sincerely thank the Editorial Team of IJMMM for their hard work to get the publication of special issue.

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