Oxygen Ion Oxidation Process on a Platinum Electrode in LiCl-Li_2O at 650°C

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INTRODUCTION

Production of pure metals from their oxides is an emerging technology using molten salt systems. The technology involves electrodeoxidation of metal oxides at the cathode and oxygen ion oxidation at the anode, typically in chloride salt systems.

A number of metal oxides, such as titanium oxide, niobium oxide, nickel oxide, uranium oxide, zirconium oxide, and hafnium oxide have been successfully reduced to their pure metal forms in molten chloride salt systems in laboratories [2-5]. During the electrodeoxidation process, metal oxide is loaded into the system as the cathode. An inert metal such as platinum or glassy carbon is applied as the anode. An oxygen ion donor compound, such as Li_2O or CaO, is added to the electrolyte. When a voltage, normally above 3V, is applied between the anode and cathode, the metal oxide is reduced to pure metal at the cathode and oxygen ions are released into the molten salt. The anode reaction involves evolution of oxygen gas or carbon dioxide gas, depending on the anode material used. The overall reaction for the electrodeoxidation or electrolytic reduction [3] of metal oxides is:

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\text{Metal Oxide (s)} \rightarrow \text{Metal (s)} + \text{O}_2(g) \text{ or } \text{CO}_2(g)
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Experiments were performed to investigate the mechanism of oxygen evolution on a platinum electrode in a molten LiCl at 650°C. Li_2O was charged as the oxygen ion donor, due to its high solubility and complete dissociation properties in the molten salt [6]. The purpose for this article is to present the observations and electrochemical measurements obtained from these experiments.

EXPERIMENT

The experiments and electrochemical measurements were conducted in a bench-scale apparatus. The electrochemical cell used for the experiments consisted of a stainless steel crucible fitted with an MgO liner. The inside diameter of the liner was 9.5 cm. The electrochemical cell was located in a glovebox under an argon atmosphere. The oxygen content in the glovebox atmosphere was controlled to be below 5ppm. A Solartron 1287 Potentiostat was used for experimental control and electrochemical measurements. Cyclic voltammetry and chronopotentiometry were used to study the electrochemical oxidation mechanisms of oxygen ions on the platinum surface. It was found that the oxygen evolution process included two oxidation steps when the concentration of Li_2O was below 0.5 wt% and one oxidation step when the concentration of Li_2O was above 0.5 wt%. The redox chemistry of oxygen ions in the molten electrolyte, the thin oxide film formed on the platinum surface, and kinetic parameters for the oxidation processes are discussed in this article, based on the experimental observations.

REFERENCES