

Monitoring the Electrolytic Reduction Process of Metal Oxide in the LiCl Molten Salt at 650°C

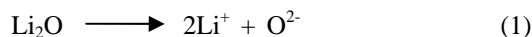
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1. Introduction

During the electrolytic reduction process of metal oxides, metal oxides are reduced in the cathode basket and oxide ions are oxidized at a platinum anode.[1,2] Basically the oxide concentration in the bulk should be maintained to be constant during the reduction process, but slow diffusion rate of oxide ions from metal oxide particles to the salt medium results in decreasing the oxide ion concentration. When a high current density is applied for the reduction, lowered lithium oxide concentration causes the platinum anode to be dissolved. To accomplish the reduction of metal oxides without serious damage of platinum anode, monitoring the lithium oxide concentration is very important [3,4]. For in-situ monitoring the oxide concentration during the reduction, cyclic voltammetry (CV) and chronoamperometry(CA) were applied.

2. Experiments and Results

Lithium oxide in a LiCl molten salt at 650°C is decomposed to give Li⁺ and O²⁻.



Decomposed oxide ions are oxidized to oxygen at the platinum anode and the resulting current should be proportional to the oxide concentration.

To monitor the oxide concentration three-electrode system is used. A tungsten wire and a platinum rod were used as a cathode and an anode, respectively. Potentials were measured with a Li-Pb alloy (Li:Pb = 1:60) reference electrode which was confined in a porous MgO tube.

2.1. Cyclic voltammetry

Fig. 1 shows the anodic cyclic voltammograms at various oxide concentrations from 0.045 to 0.926wt%. In the blank salt (0.045wt% of Li₂O), no oxidation current peak is observed up to +2.0V. However, oxidation current peaks were observed at higher oxide concentrations and current peaks shifted to negative direction with increasing the oxide concentration.

These peaks have been assigned to the following reaction:



The higher oxide concentration was favorable to form

Li₂PtO₃, the more shift anodic peak potentials were obtained.

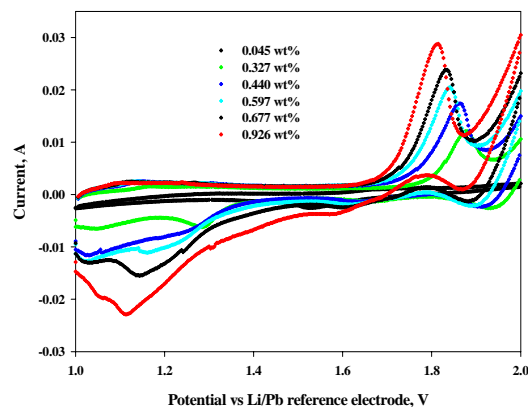


Fig. 1. Cyclic voltammograms of Pt anode at various Li₂O concentrations.

Table 1 shows the anodic peak potentials and peak currents at the various Li₂O concentrations. Peak potential shift and peak currents showed a good linear relationship with oxide concentrations.

Table 1. Anodic peak potentials and peak currents vs Li₂O concentrations (wt%)

Conc. (wt%)	0.327	0.440	0.597	0.677	0.926
Peak Potential(V)	1.876	1.862	1.841	1.832	1.800
Peak current (mA)	12.1	17.4	20.5	23.8	28.8

2.2. Chronoamperometry (CA)

Fig.2 shows anodic currents obtained for 5 seconds at +2.0 V with a CA method. When a potential step is applied to the electrode, both charging and faradaic current are obtained. The charging current, however, which is a non-faradaic current exponentially decays within several hundred milli-seconds. Since all the charging currents decay within one second, faradaic currents which are proportional to the oxide concentrations can be measured.

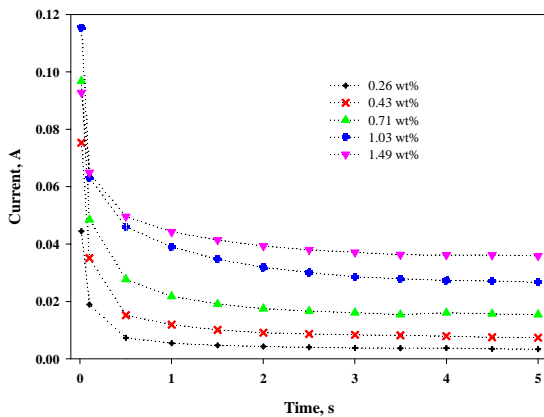


Fig.2. Anodic currents obtained for 5 seconds at +2.0V by chronoamperometry.

Fig.3 shows the relationship between the anodic currents and oxide concentrations at different measured times, 0.5, 2.0, and 5.0 seconds. It shows a relatively linear relationship up to 1wt% oxide concentration. The negative deviations at the 1.5wt% oxide concentration were assumed due to the small cathode area compared to the platinum anode.

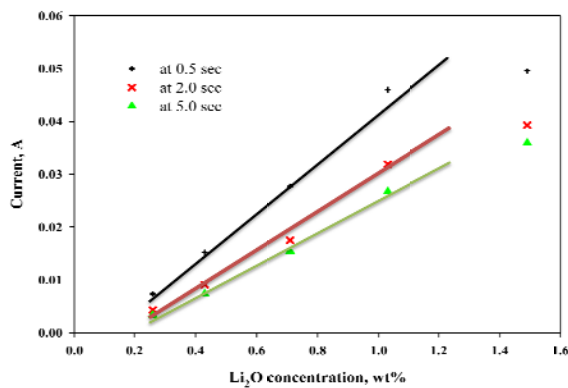


Fig. 3. Anodic current vs Li₂O concentration at various measured time.

On the contrary to other electrochemical techniques, a CA method is fast and the measured system is less disturbed. However, both a chronoamperometric method and a cyclic voltammetric method which give a good relationship between concentration and measured signals can be used to monitor the oxide concentration for the electrolytic reduction process in a LiCl molten salt at 600°C.

Reference

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