OXYGEN ION OXIDATION PROCESS ON A PLATINUM ELECTRODE IN LiCl-Li\textsubscript{2}O AT 650°C

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ABSTRACT

This report summarizes the results from an electrochemical study of the oxygen evolution process on a platinum electrode in a LiCl-Li\textsubscript{2}O electrolyte at 650°C. Cyclic voltammetry was performed at Li\textsubscript{2}O concentrations of 0.48 wt%, 0.75 wt%, and 1 wt%. The cyclic voltammograms indicated that the oxygen evolution process was a highly irreversible reaction in this system. The reaction mechanism appeared to involve a two-step electron transfer when the Li\textsubscript{2}O concentration was at 0.48 wt% and transitioned to a one step electron transfer when the Li\textsubscript{2}O concentration was increased to 0.75 wt% and 1.0 wt%. The two-step electron transfer suggests that oxygen anions, other than O\textsuperscript{2-}, may exist in the electrolyte.

INTRODUCTION

Production of pure metals from their oxides in molten salt systems is a rapidly growing technology. This technology involves electrodeoxidation of metal oxides at a cathode and oxygen ion oxidation at an anode, typically in fused chloride salt systems [1].

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 [1-6]. During the electrodeoxidation process, metal oxide is loaded into a fused salt system as the cathode. An inert metal, such as platinum, or a consumable material, such as carbon, is applied as the anode. An oxygen ion donor compound, such as Li\textsubscript{2}O or CaO, is added to the electrolyte. When a voltage 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 [7]. 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 of metal oxides can be written as:

\[
\text{Metal Oxide (s)} \rightarrow \text{Metal (s)} + \text{O}_2 (g) \text{ or CO}_2 (g) \quad [1]
\]

Extensive research has been reported on the chemistry, redox reactions, and electrode processes of oxygen or oxygen ions in molten chloride electrolytes. The results...
have been controversial due to the complexity of a four-electron process involving a $2O^2-/O_2$ couple. Furthermore, the propensity of many metal electrodes to oxidize in a fused salt system containing $O^2-/O_2$ makes it difficult to get reliable and repeatable measurements.

In this report experimental observations and electrochemical measurements of the oxygen evolution process on a platinum electrode in molten LiCl at 650°C are summarized. Li$_2$O was charged into the molten LiCl as the oxygen ion donor, due to its relatively high solubility (8.7 wt% [8]) and complete dissociation properties in the molten salt [9,10]. The purpose of this study was to examine the mechanism of oxygen evolution on platinum electrodes to support the research of electrolytic reduction of metal oxides in molten salt media at Argonne National Laboratory.

**EXPERIMENTAL**

**Equipment and Electrochemical Cell**

The electrochemical cell was designed to support high temperature experiments (650°C) with molten salts under a controlled atmosphere. The cell was operated in a furnace well within an argon-atmosphere glove box. It consisted of a working electrode, counter electrode, thermocouple, stirrer, and two reference electrodes. The cell was primarily constructed of stainless steel, but MgO- and Al$_2$O$_3$-based ceramics were used for electrical isolation. Al$_2$O$_3$ was used to isolate electrically the stirrer, while MgO was used where salt contacted the ceramic. The salt used in the experiments was placed in a 10 cm diameter by 11.3 cm high MgO crucible that sat at the bottom of the vessel. Heat shields above the salt crucible were used to prevent the upper hardware from overheating. This was necessary, since the electrodes and thermocouple were held in fixed positions using O-ring fittings (Cajon Ultra-Torr). The thermocouple used was an ungrounded type-K model. A Type SS Globe motor was used to drive the stirrer.

The working electrode was a 1-mm diameter platinum wire. Approximately 3.2 cm of the Pt wire was in contact with the electrolyte. Above the salt level, the Pt wire was tightly sleeved by a MgO tube for electrical isolation. It was expected that the real surface area of the anode might have changed during the course of experiments due to surface oxidation and possible dissolution of the platinum.

The counter electrode consisted of an empty stainless steel basket with a 2.5 cm diameter and 3.75 cm height. Similar to the Pt electrode, its shaft was electrically isolated from the heat shields by a MgO tube. Two Ni/NiO reference electrodes were installed. One was close to the Pt electrode, and the other was close to the stainless steel basket. Only the one closest to the Pt (working) electrode was used for the electrochemical measurements in this study.

**Materials**

The lithium chloride used in the study was high purity anhydrous LiCl powder purchased from Sigma-Aldrich Inc. The lithium chloride was packaged in a sealed container. Loading the salt into the crucible was conducted in the glove box. The lithium
oxide (99.6%) used for the tests was also from Sigma-Aldrich Inc. and consisted of small,
off-white chunks ranging from 1 to 10 mm in diameter. These Li₂O chunks came in a
sealed plastic bottle. The bottle was opened in the glove box and small increments were
weighed out in the glove box and added into the crucible, as prescribed. The bottle of
Li₂O remained in the glove box throughout the test period. The glove box was purged by
high purity Ar gas. The O₂ and H₂O levels were kept below 1 ppm.

Measurements

A Solartron 1287 Potentiostat was used for electrochemical measurements. Cyclic
voltammetry was conducted to study the electrochemical oxidation mechanisms of
oxygen ions on a platinum surface. Data were acquired through CorrView2 software by
Scribner Associates Inc. The voltage of the counter electrode was also monitored by an
Angilent Benchlink Data Logger and controlled by associated 34970A software (version
1.4). All the voltages reported in this paper were relative to a Ni/NiO reference electrode,
unless otherwise specified.

RESULTS AND DISCUSSION

Cyclic voltammetry was performed on the platinum electrode in molten LiCl with
Li₂O concentrations at 0.48 wt%, 0.75 wt%, and 1.0 wt%. All of the cyclic
voltammogram (CV) scans presented in this paper were (1), initiated at an open circuit
potential; (2), driven in a positive direction to an anodic vertex potential; and (3),
returned back to the open circuit potential. The open circuit potential of the Pt electrode
in the LiCl was ~ 135 mV, which was consistent with thermodynamic calculations. The
open circuit potential dropped by ~ 500 mV within ten minutes after 0.48 wt% Li₂O was
added, and drifted in a slightly more negative direction as the Li₂O concentration was
increased.

CVs at 0.48 wt% Li₂O. Figure 1 shows CVs on the Pt electrode at a Li₂O
concentration of 0.48 wt% using scan rates of 2.5, 5, 7.5, and 10 mV/sec. The anodic
vertex potential for these CV sweeps was 1.75V. The CVs in Figure 1 reveal some
distinct features. Starting from an open circuit potential, no significant current was
observed until the scanning potential reached ~ 0.7V, where a tiny current peak, PI
emerged. Based on thermodynamic calculations this current peak was attributed to the
oxidation of Pt to PtO. A reduction peak, P2, which might be related to the associated
oxidation peak, can also be seen in the negative-going scan. Peak P1 was consistent in all
the anodic CV scans performed, suggesting that a layer of PtO formed on the Pt electrode
surface prior to oxidation of oxygen ions.

As the positive-going sweep continued, an oxidation current peak, A, occurred at
a voltage from ~1.20V to 1.25V depending on the scan rate. The peak A was followed by
a more pronounced oxidation peak, B, before the oxidation current sharply increased
(more negative value) at a voltage of ~1.62V. This voltage is consistent with the
thermodynamic potential of platinum dissolution, Pt → Pt²⁺. Further extending the anodic
vertex potential resulted in a nearly linear increase in the current, indicating an electrode
reduction that was not limited by diffusion.
The next oxidation reaction, after platinum dissolution, that could occur at the Pt electrode would be chlorine evolution. The thermodynamic potential for $2CT \rightarrow Cl_2 \ (g)$ is approximately 0.265V more anodic than that for platinum dissolution. However, no such current wave was observed even when an anodic vertex potential of 2.05V was approached. Since the focus of this study was the oxygen evolution process on a platinum electrode, the anodic vertex voltages were limited to 1.70V to 1.80V to minimize Pt electrode dissolution and possible surface area changes. All the CVs presented in this report are plotted in a voltage range from 0.5 V to 1.9V for consistency.

It has been reported that Li$_2$O completely dissociates in a Li-based melt [9]. If it were assumed that O$_2^-$ was the only oxygen ion existing in the electrolyte after 0.48 wt% of Li$_2$O was added, there would be a possibility that a two-step electron transfer could occur, as is shown in Figure 1. The double oxidation peaks also suggest that an intermediate species of oxygen anions, such as O$_2^{2-}$ or O$_2^-$, may exist during the oxidation process. Although the reaction mechanism corresponding to the two oxidation peaks, A and B, could not be definitively determined, similar double oxidation peaks have been observed in the CVs performed in other electrochemical cells utilizing the same operating conditions [11]. Therefore, the CVs in Figure 1 confirmed that the double oxidation peaks, A and B, are concomitant with oxygen ion oxidation on a Pt electrode at 0.48 wt% Li$_2$O.

Figure 1 also illustrates that the voltage at which a current peak forms, namely $E_p$, varies with the scan rate. Although it is difficult to determine the $E_p$s of the A peaks, the

![Figure 1. Cyclic voltammograms of a Pt electrode in molten LiCl with 0.48 wt% Li$_2$O.](image)
Figure 2. Cyclic voltammograms for a Pt electrode in molten LiCl with 0.75 wt% Li$_2$O

Figure 3. Cyclic voltammograms for a Pt electrode in molten LiCl with 1.0 wt% Li$_2$O
$E_p$s of the B peaks clearly show a scan rate dependence, indicating the irreversible nature of the electron transfer process.

CVs at 0.75 wt% and 1.0 wt% Li$_2$O. Figures 2 and 3 are CVs on the Pt electrode at different scan rates for Li$_2$O concentrations of 0.75 wt% and 1.0 wt%, respectively. Double oxidation peaks were not observed in CVs of 0.75 and 1.0 wt% Li$_2$O, as they were in CVs of 0.48 wt% Li$_2$O. The CVs in Figures 2 and 3 consistently show a well developed oxidation peak, named Peak C, which undoubtedly is attributed to oxygen evolution and occurred in all the positive-going scans. The absolute value of Peak C increased with increasing Li$_2$O concentration and scan rate. The current/voltage relationship for Peak C also reflects a high degree of irreversibility of the single step electron transfer process.

![Figure 4](image)

Figure 4. Impact of agitation on cyclic voltammograms for a Pt electrode in molten LiCl with 1.0 wt% Li$_2$O.
Figure 5. Cyclic voltammogram on a Pt electrode in LiCl with varying Li$_2$O concentration

**Impact of Agitation.** The impact of agitation on the oxygen evolution process was also examined. This is of importance in determining the controlling step for the electrolytic reduction of metal oxide in the molten electrolyte. Cyclic voltammetry was performed at different Li$_2$O concentrations when the electrolyte was agitated by stirring the paddle at 50 rpm. It appeared that agitation had little impact on the CVs when Li$_2$O concentrations were 0.75 wt% and 1.0 wt%. Representative CVs showing such results are given in Figure 4. The CVs obtained when the Li$_2$O concentration was at 0.48 wt% and stirring at 50 rpm showed the double oxidation peaks in the positive-going scans, but the absolute values of the current peaks between the stirred and unstirred conditions were not as reproducible as those obtained at higher Li$_2$O concentrations. The reason for this variation in the peak current values at low Li$_2$O concentration is under study.

**Analysis and Discussion.** For comparison, CVs on the Pt electrode under three different Li$_2$O concentrations at a common scan rate of 2.5 mV/sec are plotted in Figure 5. CVs in this Figure demonstrate that the oxygen evolution on a Pt electrode in the system involved different electron transfer mechanisms when the Li$_2$O concentration was increased from 0.48 wt% to 0.75 wt%. Apparently the oxygen evolution was a one-step electrochemical reaction when the Li$_2$O concentration was at 0.75 wt% and 1.0 wt%, and an electrochemical reaction with at least two stages took place on the electrode when the Li$_2$O concentration was at 0.48 wt%.
The study of chemical species of oxygen that can exist in molten chlorides, and their behavior, is a remarkably difficult area in which there has been a great deal of work but no clear consensus has been emerged. The possible electrochemically active species are oxide ion, O$_2^-$, peroxide ion, O$_2^{2-}$, superoxide, O$_2^-$, and molecular oxygen. It is generally agreed that the solubility of molecular oxygen is low enough that this species can be neglected [12]. It was reported that the Nemst slopes of Pt-oxygen electrodes were dependent only on the equilibrium concentration of oxide ion by the following equation [9]:

$$\frac{1}{2} \text{O}_2 + \text{O}_2^- \rightarrow \text{O}_2^{2-}$$  \[2\]

If O$_2^-$ is the predominant species, the Nemst slope should reflect $n = 2$ due to the following mechanism:

$$\text{O}_2^- \rightarrow \frac{1}{2} \text{O}_2 + 2e^-$$  \[3\]

If the Nemst slope corresponds to $n = 1$, then O$_2^{2-}$ may predominate as per the following equation:

$$\text{O}_2^{2-} \rightarrow \text{O}_2 + 2e^-$$  \[4\]

Reference [9] reported that $n$ was 2 at low oxide concentrations and becomes equal to 1 at higher oxide concentrations. The presence of O$_2^{2-}$ and O$_2^-$ in molten alkali nitrate media has also been proven [13]. The findings from this study are in agreement with these
previous studies. Oxygen anions, other than O$_2^-$, may exist in the LiCl/Li$_2$O at 650 °C when the Li$_2$O concentration is varied.

The key to understanding the reaction mechanisms represented by the cyclic voltammograms is to determine the number of the electron(s) involved in each transfer step [14]. To this end, the peak current density versus square root of the scanning rate was plotted for the CVs at varying Li$_2$O concentrations. Figure 6 illustrates that the peak current densities at different Li$_2$O concentrations are all straight lines and proportional to the square root of the scan rate, indicating the reliability of the measured data. Determination of the reaction mechanisms at different Li$_2$O concentrations is underway at this writing.

The significance of oxygen anions other than O$_2^-$ in a fused salt system is the potential negative impact on the cathode process for an electrolytic reduction of metal oxides. If it were assumed that peroxide ions existed in the electrolyte, then the reduction reaction, O$_2^{2-} + 2e^- \rightarrow 2O^2-$, may occur at the cathode at a less negative potential than that for metal oxide reduction. Such a mechanism could contribute to low current efficiencies, which have been observed in electrolytic reduction systems [15].

CONCLUSIONS

A cyclic voltammetry study confirmed that the oxygen evolution process on a platinum electrode in a LiCl/Li$_2$O system at 650°C involved different electron transfer steps when the Li$_2$O concentration changed from 0.48 wt% to 0.75 wt%, which suggested that ionic species other than O$_2^-$ may have existed in the electrolyte.

This observation is in agreement with previous studies, where O$_2^-$ is the predominant species in molten chloride salt when Li$_2$O concentration is low and O$_2^{2-}$ is predominant when Li$_2$O is concentration is high.

The presence of peroxide or superoxide ions in the electrolyte may have a negative impact on the cathode process when using a molten salt electrolytic de-oxidation technique to reduce metal oxides.

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