

In-line Monitoring of an Oxide Ion in LiCl Molten Salt Using a YSZ Based Oxide Ion Selective Electrode

**Young-Hwan Cho, Jong-Seon Jeon, Jei-Won Yeon,
In-Kyu Choi, and Won-Ho Kim**

Korea Atomic Energy Research Institute
150 Deokjin-dong, Yuseong-gu, Daejeon, Korea, 305-353
yhcho@kaeri.re.kr

(Received November 18, 2003)

Abstract

The electrode potential characteristics of a YSZ based membrane metal oxide electrode have been studied in molten LiCl at 700°C by the potentiometric method. The electrode exhibited a good potential response to $\log[\text{O}^{2-}]$ and data reproducibility. The calibration plot (potential vs. $\log[\text{O}^{2-}]$) was found to be linear, obeying the Nernst equation. The electrode potential showed a good reversibility corresponding to increase/decrease of the oxide ion present in the molten LiCl. The physical and chemical durability appeared to be sound after several repeated uses, resulting in reproducible results. However, "the proposed electrode" failed when metallic Li was present in the melt.

Key Words : electrode, molten salt, oxide ion, potentiometry

1. Introduction

Recently, ionic melts have become attractive reaction media in many fields.[1,2] Molten salt based electrochemical processes have been proposed as a promising method for future nuclear programs and more specifically for spent fuel processing.[3,4,5] During the course of these electrochemical processes, the generation of oxygen gas is involved, thus acting as a key process parameter. Accordingly, a technology for monitoring oxide ion concentration in the ionic melt is required. Amongst the several methods of

oxide ion measurement, a continuous and in-situ monitoring technique using a suitable electrode system would be the most appropriate.[6,7] However, little study has been conducted in a molten salt medium at high temperature. The present study is focused on the in-line determination of oxide ion concentration using an ion selective membrane metal oxide electrode, NiO | ZrO₂(Y₂O₃). Molten LiCl has been chosen as the electrolyte medium because many important pyrochemical processes are carried out in LiCl based molten salt media.

2. Experimental

2.1. Electrode and Apparatus

The membrane metal oxide electrode consists of a nickel oxide inner electrode placed into an outer ceramic membrane (YSZ membrane) made of zirconia (ZrO_2) stabilized by yttria (Y_2O_3) doping. An Ag/AgCl electrode was used as a reference (See Figure 1). Yttria stabilized zirconia (YSZ) provides ideal oxide ion conduction as well as a

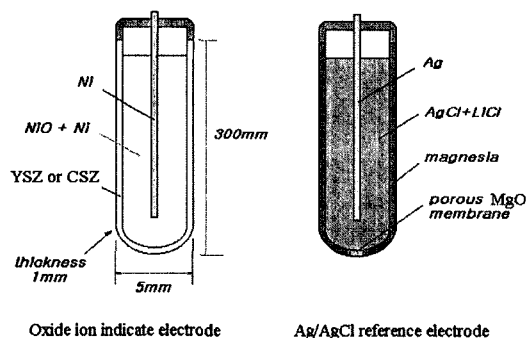


Fig. 1. Membrane Metal Oxide Electrode and Reference Electrode

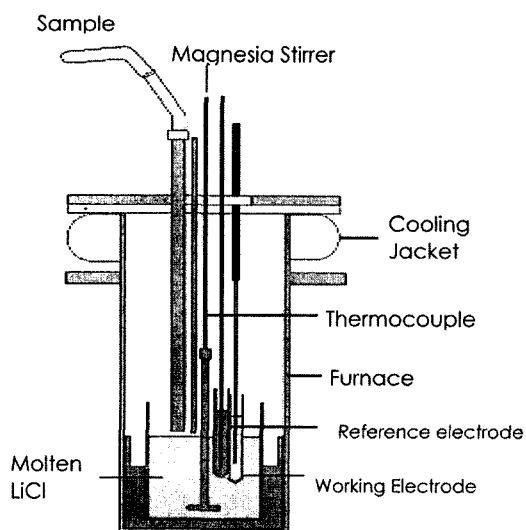


Fig. 2. Apparatus for Electrochemical Measurements in Molten LiCl

dense membrane environment for protecting the inner electrode parts.[8] The electrode was designed by the authors and was fabricated by Woojin Inc. in Korea.

Electrochemical measurements were carried out using a EG&G potentiostat model 273A interfaced with a PC. The experimental apparatus is presented in Figure 2.

2.2. Experimental Procedure

All the experiments have been carried out in a moisture & oxygen gas controlled glove box. A dry argon atmosphere was maintained inside the glove box. 500 g of lithium chloride was placed in a stainless steel crucible and electrically insulated by an MgO crucible. The crucible was heated slowly and kept at 700°. Li_2O was added to this melt to make 0.1, 0.2, 0.5, 1.0, 2.0, and 4.0 percent Li_2O in weight, successively, and the potential change was monitored at each step. Here, the oxide ions were added by inserting known amounts of Li_2O . According to our solubility measurements, Li_2O dissolves in molten LiCl at 700°... up to ca. 8 weight percent. Dissolved Li_2O dissociates completely to produce an oxide ion (O^{2-}) when the solubility is less than 4 weight percent.

3. Results and Discussion

3.1. Electrode Potential Response to Oxide Ion Concentration

Linear relationship between the electrode potential and $\log[O^{2-}]$: The electrode potential of the metal oxide electrode can be expressed as the following Nernst type equation.

$$\psi_{Me^{2+}} = \psi^0_{Me^{2+}} - \frac{2.3RT}{2F} \log a_{O^{2-}} \quad (1)$$

The net reaction is $Ni^{2+} + O^{2-} \rightarrow NiO$ (2)
 Therefore, the plot of the potential vs. the logarithm of the oxide ion concentration $[O^{2-}]$ in molten salt is expected to be linear with a slope of $-2.3RT/2F$ (92 mV/1 order concentration change) for a metal oxide electrode obeying the Nernst Equation.(Equation 1)

The electrode potential was plotted vs. the logarithm of the added oxide ion (in weight percent), and the results are presented in Figure 3. They display a good linear relationship as predicted by the Nernst equation in the range of Li_2O up to ~4 weight percent. In an actual electrochemical process occurring in a molten LiCl medium, the maximum amount of dissolved Li_2O is less than 4 weight percent. The linear relationship up to 4 weight percent satisfied the requirements for this electrode to be used for the in-line monitoring of an oxide ion.

Reversibility of the electrode potential: In addition to linearity of the electrode potential vs. $\log[O^{2-}]$, the electrode potential showed a reversible change when responding to increases and decreases of oxide concentration. For this experiment, separate batches of molten LiCl

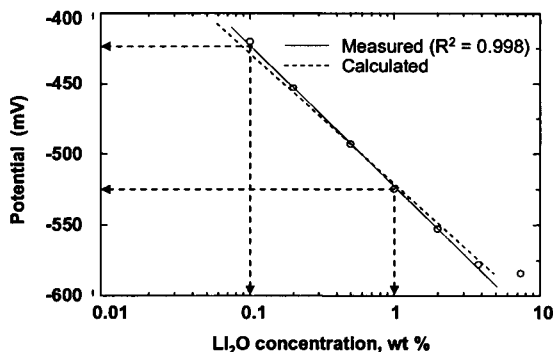


Fig. 3. Plot of the Electrode Potential (vs Ag/AgCl $\log[O^{2-}]$)

containing 0.005, 0.5, and 2 weight percents of Li_2O were prepared and the electrode potential was measured individually, successively, and repeatedly, with the same electrode. Figure 4 presents the results, which suggest that the electrode potential responds linearly and reversibly to increase and decrease of the $\log[O^{2-}]$.

3.2. Reproducibility of the Data and Physical Integrity

In order to be used as an indicator electrode in process monitoring, reproducibility of the electrode potential data is essential. Also, as it operates under high temperature and severe chemical conditions, the electrode should be physically and chemically durable. According to the results from several batches of experiments with the same electrode after repeated use, the linearity of the potential vs. the $\log[O^{2-}]$ was fully confirmed. Figure 5 presents the results of this experiment. Here, the intercept of the line may vary in each experiment depending on the amount of residual O^{2-} in LiCl. Even a very small difference in the amount of residual O^{2-} may change the intercept value significantly, depending on the

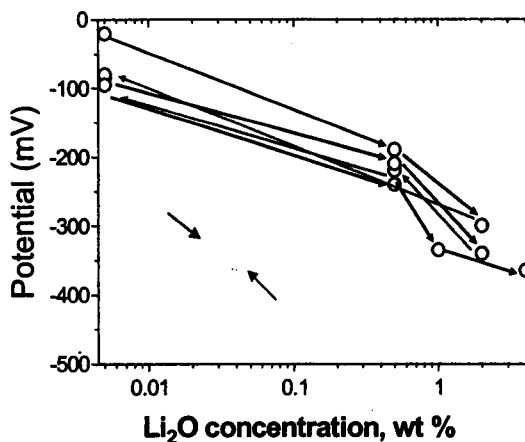


Fig. 4. Reversibility of the Electrode Potentials Pondering to the Change of the $\log[O^{2-}]$

conditions of the glove box and the reagent purity. The performance of the electrode was tested for 48 hours while immersed in molten LiCl at 700°C, and there was no failure in the electrode characteristics. Even in the presence of a highly reactive Li metal that was dissolved up to its solubility limit, the electrode apparently maintained its physical integrity. These results suggest that the membrane metal oxide electrode, NiO|ZrO₂(Y₂O₃), may be used as an indicator electrode for monitoring processes occurring in various ionic melts where oxide ion (O²⁻) acts as a key parameter.

3.3. Limitations

There are two main limitations in monitoring the variations of Li₂O using this electrode. One is that the electrode potential linearity vs. the log[O²⁻] starts to deviate slightly when the Li₂O concentration is more than 4 weight percent, because of incomplete dissociation. However, as the concentration of Li₂O is less than 4 weight percent in most real processes, this does not constitute a serious problem for actual

applications.

The other limitation is metallic Li in molten LiCl. The presence of dissolved lithium metal may cause side reactions affecting the performance of the indicator electrode. In the case of the present study, it shifted the electrode potential significantly to positive values by causing an electrochemical reaction that is not clearly understood. This phenomenon may be attributed to its small size and high reactivity in molten LiCl. Because of these properties, metallic Li may pass through the YSZ membrane and thereupon cause an undesirable electrode reaction. Also, metallic Li is known to be intercalated into carbon based materials in molten salts.[9] Such potential adverse effects need to be identified and should be overcome for the reliable monitoring of oxide ion concentration in molten salt in the presence of a dissolved lithium metal. Therefore, the electrode developed in this study is not applicable to processes where metallic Li is present in the molten salt. Presently, related studies to overcome this drawback are underway.

4. Conclusions

The electrode potential characteristics of a YSZ based membrane metal oxide electrode (NiO|ZrO₂(Y₂O₃)) were studied in molten LiCl at 700 °C by the potentiometric method. The electrode exhibited a good potential response to log[O²⁻] and data reproducibility. The calibration plot (potential vs. log[O²⁻]) was found to be linear, obeying the Nernst equation within a range of Li₂O content up to ~4 weight percent. The electrode potential showed good reversibility corresponding to increase/decrease of the oxide ion in molten LiCl. The physical and chemical durability appeared to be sound after several repeated uses, resulting in reproducible results. However, the proposed electrode has some

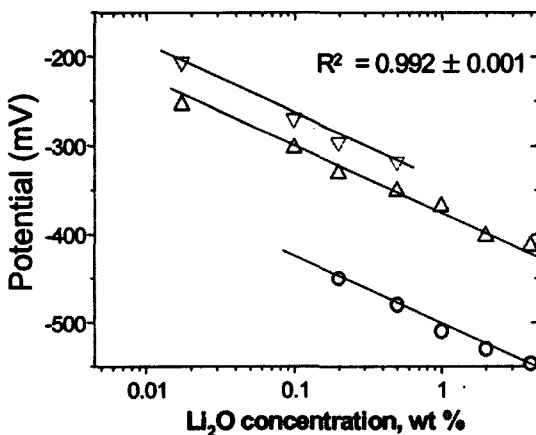


Fig. 5. Reversibility of the Electrode Potential Responding to the Change of the Log[O²⁻] After Several Repeated Uses

limitations, namely, it is not applicable when metallic Li is present in the melt.

Acknowledgements

This study was supported by the Mid- and Long-Term Atomic Energy R&D Fund of the Korean Ministry of Science and Technology.

References

1. Kenneth R. Seddon, "Ionic Liquids for clean technology" *J. Chem. Tech. Biotechnol.* 68, 351-356 (1997).
2. Derek. J. Fray, "Emerging molten salt technologies for metals production" *J. of Metallur.* 26-31 (2001).
3. T. Usami , M. Kurata , T. Inoue, H.E. Sims, S.A Beetham., J.A. Jenkins, "Pyrochemical reduction of uranium dioxide and plutonium dioxide by lithium metal". *J. Nuclear Materials.* 300, 15-26. (2002).
4. OECD/NEA, "Actinide and fission product partitioning and transmutation", Proceedings of seventh information exchange meeting held at Jeju, Republic of Korea, 14-16 October 2003, ISBN 92-64-02125-6, EUR20618 EN (2003).
5. B. H. Park, J. M. Hur, C. S. Seo, and S. W. Park, "A study on the electrochemical reduction of uranium oxide in a LiCl-Li₂O molten salt", Proceedings of Global 2003 Conference, New Orleans, Louisiana, Nov. 16 - 20 (2003).
6. V.L. Cherginets, "Oxide ion electrode and oxide ion donors in molten alkaline halogenides. A consideration of potentiometric studies", *Electrochim Acta* 42, 1507-1514 (1997).
7. V.L. Cherginets, T.P. Rebrova, "Studies of some acid-base equilibria in the molten eutectic mixture KCl-LiCl at 700°C" *Electrochimica Acta* 45, 469-476 (1999) and references there in.
8. J. C. Boivin and G. Mairesse, "Recent Material Developments in Fast Oxide Ion Conductors" *Chem. Mater.*, 10, 2870-2888 (1998).
9. Q. Xu, C. Schwandt, G. Chen, D. Fray, "Electrochemical investigation of lithium intercalation into graphite from molten lithium chloride", *J. Electroanal. Chem.* 530, 16-22 (2002).