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Determination of oxide ion activity in molten LiCl using oxide ion electrode

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Abstract

The linearity and the reproducibility of the membrane oxide electrode potential for oxide ion activity have been testified in molten LiCl at 700 ^{o}C by the potentiometric method. Experimental detail has been described. The calibration curve (potential vs log[O^{2-}]) has been found to be linear. The physical, chemical durability appeared to be sound after repeated use, resulting in reproducible results.

1. Introduction

A molten salt based electrochemical process is proposed as a promising method for spent nuclear fuel processing[1,2]. During the course of the process, lithium oxide (Li_2O) is produced and the monitoring of the corresponding oxide ion concentration, activity of O^{2-}, in the melt is required. Amongst the several methods, continuous and *in-sit*u monitoring technique using suitable electrode system would be the most suitable one[3]. However, little study has been done in molten salt medium at high temperature. The present study is focused on the in-line determination of oxide ion activity using the membrane metal oxide electrode, $NiO|ZrO_2(Y_2O_3)$.

2. Experimental

The membrane metal oxide electrode consists of nickel oxide inner electrode placed into a outer ceramic membrane (YSZ membrane) made of ZrO_2 stabilized by Y_2O_3

doping(YSZ). Ag/Agcl electrode was used as a reference. (See Figure 1)

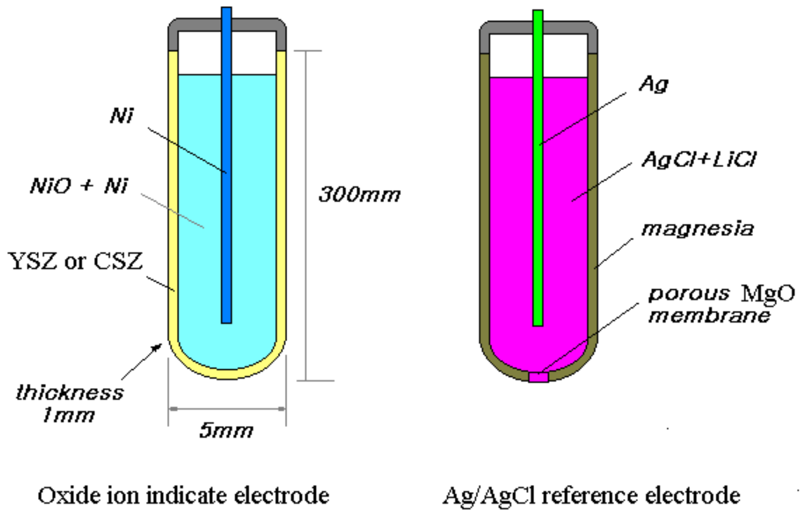

Figure 1. Membrane metal oxide electrode and reference electrode

All the experiments have been carried out in the moisture & oxygen controlled glove box. Inside of the glove box was kept under a dry argon atmosphere. Electrochemical measurements were carried out using a EG&G potentiostat model 273A interfaced with a PC. A 500 g of lithium chloride was placed in carbon crucible and electrically insulated by MgO crucible. The crucible was heated slowly and kept at 700 ^oC, and 0.1, 0.2, 0.5, 1.0, 2.0, 4.0 in weight percent Li2O was added, successively and potential change was monitored. The experimental apparatus was presented in Figure 2.

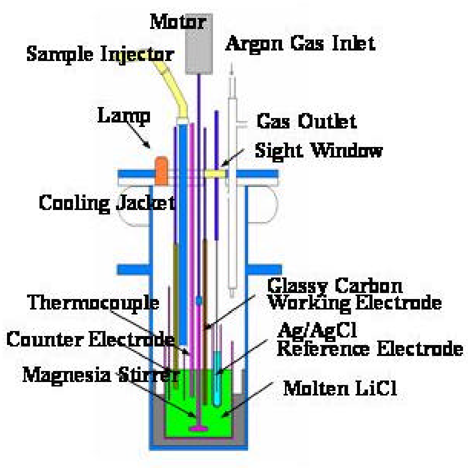

Figure 2. Experimental Apparatus for electrochemical measurements in molten salt.

3. Results and Discussion

The electrode potential of the metal oxide electrode can be expressed as the following Nernst type equation.

$$y\,Me^{2+} = y\,{}^{0}Me^{2+} - \frac{2.3RT}{2F}\log aO^{2-}$$

The net reaction is $Ni^{2+} + O^{2-} \rightarrow NiO$.

Therefore, the plot of potential, y , vs logarithm of oxide ion activity, $[O^{2-}]$, in the molten salt is expected to be linear for metal oxide electrode.

The electrode potential was plotted vs logarithm of oxide ion (in weight percent) added, and the results are presented in Figure 3. They showed good linear relationship as expected. In order to be used as an indicator electrode in the process monitoring, reproducibility of the electrode potential data is essential. According to the results from several batches of experiments, the linearity of the potential vs log[O^{2-}] was fully confirmed.

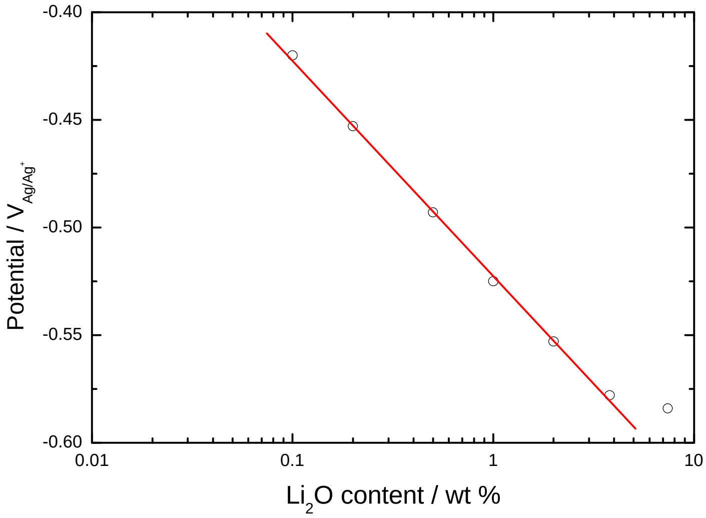

Figure 3. Plot of electrode potential vs ln[O^{2-}]

This means that membrane metal oxide electrode, NiO|ZrO_2(Y_2O_3), may possibly be used as an indicator electrode for monitoring lithium oxide concentration during the pyrochemical process of spent nuclear fuel in molten salt. However, some problems still remain. The presence of dissolved lithium metal may cause side effects affecting the performance of the indicator electrode. It may shift the electrode potential by certain electrochemical reaction. Moreover, it is known to be intercalated into carbon based materials[4]. From our preliminary results, the presence of lithium metal not cause significant side effetcs. At any rate, these adverse effects, if exist, needs be identified and should be overcome for the reliable monitoring of oxide ion activity in molten salt in the presence of dissolved lithium metal. Presently, related studies are underway.

4. Conclusions

The possibility of the use of membrane oxide electrode, NiO|ZrO_2(Y_2O_3), for the monitoring of the oxide ion activity in molten salt at high temperature has been suggested. The electrode potential *vs* log[O^{2-}] exhibited a linear relationship with reproducibility. The physical and chemical durability was found to be sound after repeated use. However, it needs to be testified in some more severe conditions.

Acknowledgement

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