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Journal of Nuclear Materials 375 (2008) 275–279

journal of nuclear materials

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Application of a chronoamperometric measurement to the on-line monitoring of a lithium metal reduction for uranium oxide

Tack-Jin Kim [a], Young-Hwan Cho [a], In-Kyu Choi [a], Jun-Gill Kang [b],
Kyuseok Song [a,*], Kwang-Yong Jee [a]

[a] *Nuclear Chemistry Research Center, Korea Atomic Energy Research Institute, Dukjin-Dong 150-1, Yuseong, Daejeon, Republic of Korea*
[b] *Choongnam National University, Daejeon 305-764, Republic of Korea*

Received 19 July 2007; accepted 27 December 2007

Abstract

Both a potentiometric and a chronoamperometric electrochemical technique have been applied in an attempt to develop an efficient method for an on-line monitoring of a lithium metal reduction process of uranium oxides at a high-temperature in a molten salt medium. As a result of this study, it was concluded that the chronoamperometric method provided a simple and effective way for a direct on-line monitoring measurement of a lithium metal reduction process of uranium oxides at 650 °C by the measuring electrical currents dependency on a variation of the reduction time for the reaction. A potentiometric method, by adopting a homemade oxide ion selective electrode made of ZrO_2 stabilized by a Y_2O_3 doping, however, was found to be inappropriate for an on-line monitoring of the reduction reaction of uranium oxide in the presence of lithium metal due to an abnormal behavior of the adopted electrodes. The observed experimental results were discussed in detail by comparing them with previously published experimental data.

PACS: 28.41.Kw; 61.20.Qg; 07.07.Df; 82.80.Fk

1. Introduction

Molten salts have become an attractive reaction media in many research fields and industrial applications such as a metal production (e.g. Li, Al, etc.) from metal oxides and processing of a spent nuclear fuel in recent years [1–3]. Molten salt based pyro-chemical processing technique has been proposed as one of the promising techniques for future nuclear related research and development, and more specifically for a spent fuel processing [4–8]. Accordingly, a molten salt process, which can remove fission products from a resultant uranium product following a reduction of a spent oxide fuel to a uranium metal, has been developed for recycling uranium as either a nuclear fuel or disposing of the uranium as intermediate- or low-level radioactive wastes.

One of the useful chemical reactions from recycling a uranium fuel, a lithium metal reduction process of a uranium oxide by the use of lithium metal in the presence of a molten salt at a high-temperature (so called, lithium metal reduction process) [9,10], is represented as reaction (1):

$$U_3O_8 + 16Li \rightarrow 3U + 8Li_2O \qquad (1)$$

During the course of this chemical process, oxide ions which act as a key process parameter during the reduction process can be generated due to the reasonable solubility (~8.7 wt%) of the Li_2O. Therefore, a monitoring of the concentration of the oxide ions in the molten salt at a high-temperature can be an efficient way of controlling a lithium metal reduction process. Among the available techniques for monitoring oxide ions, a continuous and on-line monitoring technique by using an appropriate electrode

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[*] Corresponding author. Tel.: +82 42 868 8226; fax: +82 42 868 8148.
E-mail address: sks@kaeri.re.kr (K. Song).

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doi:10.1016/j.jnucmat.2007.12.002

system has been suggested as the most promising one, as discussed in previous reports [11,12]. However, few studies on the monitoring of an oxide ion in a molten salt medium at a high-temperature are available. Iizuka et al. reported on the application of a normal pulse voltammetry to an on-line monitoring of actinide concentrations in a molten salt electrolyte [13]. But they did not investigate the applicability of the developed techniques for a reaction process involving insoluble samples, such as uranium oxide. Therefore, it is necessary to develop an efficient process monitoring technique for reactions involving insoluble samples in a molten salt by measuring other available reaction parameters such as the concentration of the oxide ions.

In the present study, we present the first demonstration of an on-line monitoring technique for a lithium metal reduction process by adopting both potentiometric and chronoamperometric methods. The application results of these two monitoring techniques as well as the characteristic behaviors of the adopted reduction reaction are presented.

2. Experimental

2.1. Electrochemical systems

2.1.1. Potentiometric measurements

A typical method for measuring an amount of oxide ions is to measure an electrode potential by using an oxide ion selective electrode. In the present study, a membrane type ion sensing electrode and Ag/AgCl electrode were used as an ion monitoring electrode and reference electrode [14], respectively, as shown in Fig. 1. The adopted oxide ion monitoring electrode was developed by the authors by placing a nickel rod and nickel oxide inside a Yttria Stabilized Zirconia (YSZ) membrane made of ZrO_2 stabilized by an Y_2O_3 doping. The YSZ was adopted because it can provide an adequate environment for a selective sensing of oxide ions without causing any damage to the inner part of the electrode's system. As was discussed in the introduction section of the present paper, lithium oxides produced in reaction (1) dissolve in a lithium chloride molten salt at 650 °C by up to an 8.7 wt% [9] and these dissolved lithium oxides completely dissociate to produce oxide ions (O^{2-}). Therefore the reduction process of uranium oxide can be monitored by measuring the concentration of the oxide ions with an oxide ion selective electrode, in this case YSZ. The net reaction of the reduction reaction for uranium oxide, occurring at an ion monitoring electrode, can be expressed as follows;

$$Ni + O^{2-} \rightarrow NiO + 2e^- \qquad (2)$$

Electrochemical measurements were carried out by using an EG&G ORTEC potentiostat (model 273A) interfaced with a computer as described in reference [14] in order to the measure concentration of the oxide ions in reaction (2).

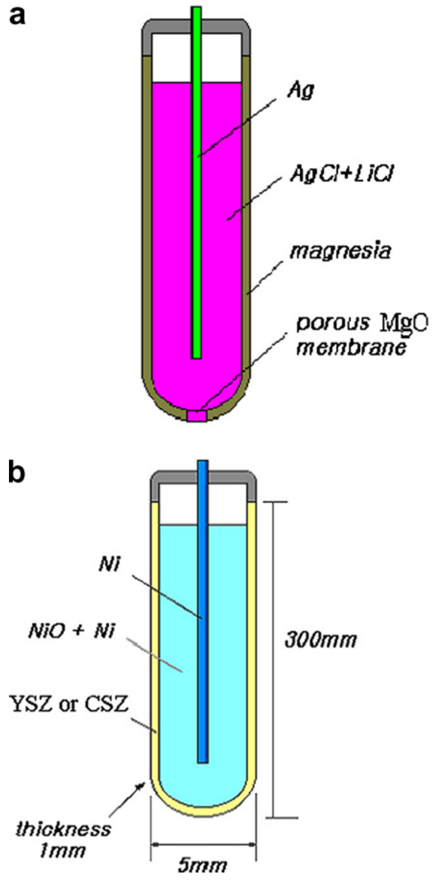

Fig. 1. Schematic diagram of the (a) Ag/AgCl reference electrode and (b) oxide ion indicate electrode.

2.1.2. Chronoamperometric measurements

An alternative method for a process monitoring of reaction (1) is to measure the electrochemical parameters for reaction (3) which are an oxidation of dissociated oxide ions and a reduction of dissociated lithium ions. Conventional potentiostat/galvanostat and a reactor system for melting molten salts were adopted to monitor reaction (3).

$$\begin{aligned} &\text{Anode}: O^{2-} \rightarrow 1/2O_2 + 2e^- \\ &\text{Cathode}: Li^+ + e^- \rightarrow Li^0 \qquad (3) \end{aligned}$$

Fig. 2 schematically describes the chronoamperometric measurement system adopted in the present study. The system includes a two electrode system, an anode and a cathode, connected to a potentiostat/galvanostat, used for measuring the cathodic current at an electrostatic potential which reduces the lithium ion to lithium metal at the cathode (−).

2.2. Experimental procedure

All the experiments have been carried out in a moisture and oxygen controlled glove box. The lithium metal reduction process has been carried out on a small scale.

Three hundred gram of lithium chloride (LiCl) and 31.6 g of uranium oxide (U_3O_8) were introduced into a nickel reactor, then the temperature of the reactor was

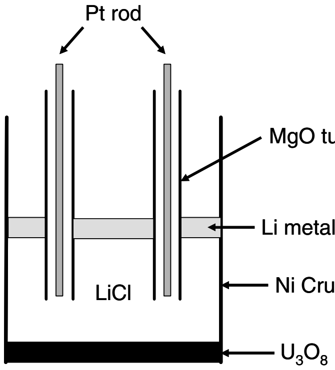

Fig. 2. Apparatus for the chronoamperometric measurement of the lithium reduction reaction in a molten salt environment.

increased to 650 °C under an argon gas atmosphere in order to melt the lithium chloride. Platinum rods were used as an anode as well as a cathode. This electrode system was placed in the molten salt reactor and connected to a potentiostat/galvanostat. Subsequently, 7 g of lithium metal was further added to the reactor in order to generate a lithium metal reduction environment, and the cathodic current variation dependency on the reaction time was continuously measured at an electrostatic potential of 2.0 V. For a potentiometric measurement, a selective oxide ion electrode made of YSZ was used as described in Ref. [14].

3. Results and discussion

3.1. Potentiometric approach

Fig. 3(a) is a plot of the electrode potential measured by a YSZ electrode according to the logarithmic value of the added oxide ion (in weight percent) by a variation of the concentration of the lithium oxide. As shown in Fig. 3(a), the linear dependency of the electrode potential indicates that the YSZ electrode provided a good inverse linearity. Based on this experimental result, we applied this electrode system to measure the electrode potential of a lithium metal reduction process. The measured electrode potential according to the reaction time is plotted in Fig. 3(b). The measured electrode potential, however, increased exponentially as a function of the reaction time, which is contrary to the behavior from the result shown in Fig. 3(a). This observation of an opposing behavior for the electrode potential may be attributed to the presence of lithium metal which was not contained in the reaction system presented in Fig. 3(a). The presence of lithium metal in the lithium chloride molten salt unusually induces various side reactions, such as a lithium penetration [15]. Some oxide materials in YSZ can be reduced by Li metal, generating Li_2O as a reaction product. For example, ZrO_2 in YSZ may be spontaneously reduced by Li metal by following reaction:

$$4\mathrm{Li} + \mathrm{ZrO_2} = 2\mathrm{Li_2O} + \mathrm{Zr}$$
$$\Delta G = -27.576\ \mathrm{KJ} \quad \text{at } 650\,^\circ\mathrm{C}$$

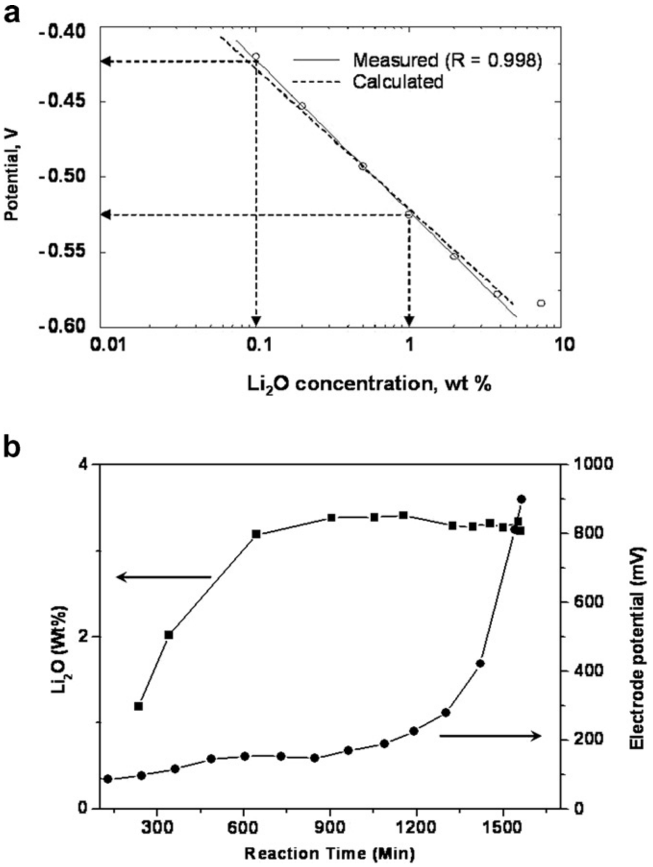

Fig. 3. (a) Measured electrode potential corresponding to the changes in Li_2O in the absence of Li metal and (b) electrode potential measured during each step of the Li metal reduction process.

Thermodynamically this reaction can occur. Therefore ceramic materials cannot be used as structural materials in the Li metal reduction process. This serious side effect may be attributed to the small size and extremely high reactivity of the lithium metal in the molten salt medium as discussed in Ref. [15]. The lithium metal may have passed through the YSZ membrane and caused an undesirable reaction at the electrodes. According to a previous report by Xu et al. even carbon based materials were attacked by lithium metal to intercalate in molten salts due to its reactive characteristics [16]. We, therefore, conclude that the developed YSZ electrode can be used for monitoring a reduction process where metallic lithium is not present in a lithium chloride molten salt.

3.2. Chronoamperometric approach

Since the potentiometric approach was not appropriate for monitoring a lithium metal reduction process of uranium oxide in a molten salt medium due to the presence of lithium metal, a chronoamperometric approach was applied as an alternative technique. When uranium metal and lithium oxide are produced through a reaction between uranium oxides (UO_x, $x \leqslant 3$) and lithium metal in a lithium chloride molten salt at 650 °C the reduction yield of the uranium metals from the uranium oxides can be measured by monitoring the concentration of the oxide ions by a chronoamperometric method. The chronoamperometric measurement is characterized in that (1) lithium oxide is dissolved in lithium chloride upon a reduction process of reaction (1) and (2) an electrolysis to reduce the dissociated lithium ion to lithium metal is applied directly. We can expect from reaction (1) that the amount of lithium oxide will increase accordingly as the rate of uranium metal production is increased. In other words, the cathodic current resulting from the electrolysis of lithium oxide increases in proportion to the amount of produced uranium metal.

Meanwhile, the electrolysis of the molten salt of pure lithium chloride may result in a more negative potential (−3.0 V) by generating chlorine gas and lithium metal when compared to the case where lithium oxide is present (−2.0 V). If the lithium oxide is present in addition to the molten salt of lithium chloride, oxygen gas can be generated, instead of chloride gas, due to the potential difference of ~1.0 V. Therefore, we can conclude that the presence of lithium oxide initiated the reaction to produce lithium metal, even at a cell potential of −2.0 V. As a result, the cathodic current at which the lithium metal is produced becomes higher as the amount of lithium oxide increases. Hence, the reduction yield of the uranium metal from the uranium oxides can be determined by measuring the cathodic current according to the amount of produced lithium oxide as a by-product. Fig. 4 shows the cathodic current measured for the reduction process of U_3O_8 in the presence of lithium metal. The concentration of the lithium oxide, represented by the cathodic current, shows a maximum value at 20 h of the reduction time due to a completion of the reduction of the uranium oxide. Moreover, the cathodic current decreases after 20 h of the reduction process due to a decrease of the concentration of the lithium oxide caused by a further reduction of the lithium oxides. This observation indicates that the uranium oxide is completely reduced to its corresponding metal, U at ~20 h of the reduction process. Baseline run of the oxide reduction in the absence of Li metal with U_3O_8 produced no appreciable cathodic current, showing flat baseline with cathodic current below 0.05A. This shows that the cathodic current in Fig. 4 is a contribution from a Li_2O produced by U_3O_8 reduction.

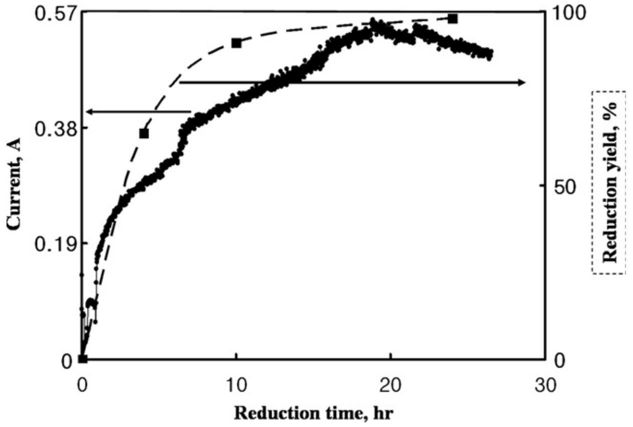

Fig. 4. Chronoamperometric measurement at −2.0 V during the U_3O_8 reduction by Li metal in molten LiCl at 650 °C. (■ is the reduction yield reported by RIAR while ● is the experimental data obtained in the present study).

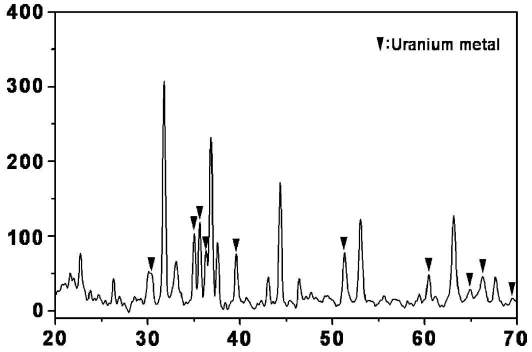

Fig. 5. XRD diffractogram of the final reaction product.

Fig. 4 also contains data observed by scientists at RIAR's (Research Institute for Atomic Reactors) [17] by measuring the reduction yield with a conventional wet analytical method (off-line). As can be seen from Fig. 4, our data measured by an on-line monitoring method closely resembles RIAR's data which was measured by an off-line conventional wet analytical method. Therefore, the reduction yield of the uranium metal from the uranium oxide can be measured on-line by monitoring the electrical current generated due to a reduction of the lithium oxide to lithium metal. In order to confirm the present experimental results, the final product of the reduction reaction of uranium oxides was analyzed by using the X-ray diffraction technique. As can be seen from Fig. 5, the measured X-ray diffraction patterns of the final product of the reaction revealed peaks representing uranium metal. But peaks representing UO_2 and U_3O_8 were not observed. Therefore we can conclude that the reduction reaction of the uranium oxides was completed and the on-line monitoring technique by adopting a chronoamperometric measurement showed the expected results with a completion of the reaction after 20 h.

4. Conclusion

Both potentiometric and chronoamperometric methods have been applied in order to establish an appropriate on-line monitoring technique for a lithium metal reduction process of uranium oxides. The chronoamperometric method was found to be an effective on-line monitoring technique for the lithium metal reduction process of uranium oxides in lithium a chloride molten salt at 650 °C The potentiometric method, however, by using an oxide ion selective electrode was found to be in appropriate for an on-line monitoring of the reduction reaction due to the reactivity of the metallic lithium which resulted in an undesirable reaction with the metals contained in the YSZ electrode.

Acknowledgement

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

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