Can Carbon Be an Anode for Electrochemical Reduction in a LiCl-Li2O Molten Salt?

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Electrochemical reduction of UO2 in a LiCl-Li2O molten salt using a C anode was investigated. Possible reduction and oxidation reactions were characterized. UO2 was reduced to U metal but the reduction yield decreased after the repeated use of an electrolyte. CO32− formation and its decomposition to C caused the lowering of current efficiency. The problem of dissolved CO32− should be addressed for the application of C anodes for the metal production in a LiCl-Li2O molten salt.

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Electrochemical reduction of metal oxides is important for the recycling of oxide spent fuels from nuclear power plants as metal fuels for fast reactors.1–3 A LiCl-Li2O molten salt due to its high electrolytic conductivity and relatively lower melting point of 606 °C has been considered as the most suitable electrolyte for the electrochemical reduction of oxide spent nuclear fuels and UO2.

Pt anodes have been used in a LiCl-Li2O molten salt.4,5 However, Pt is expensive and unstable due to Li2PtO3 formation and Li attack.6 Therefore, many efforts have been attempted to develop alternative anodes, but with no successful results.7 The use of a C anode for the reduction of UO2 to U in a molten CaCl2-CaO was reported.8 However, employing C anodes in a LiCl-Li2O molten salt was excluded worrying about the accumulation of C dusts in the salt.

We investigated the electrochemical reduction of UO2 by using a C anode and elucidated the reactions and showed that suppression of CO32− decomposition at a cathode is the key for the success of C as an anode in a LiCl-Li2O molten salt.

Experimental

Reduction cell.— The electrochemical experiments were carried out in a high purity Ar atmosphere glove box using the same configuration cell shown in Fig. 2 of Ref. 4. A stainless steel crucible was loaded with vacuum dried 700 g of LiCl (99.99%, Aldrich) and 7 g of Li2O (99.5%, Cerac) to make a LiCl-1 wt% Li2O salt. A Li-Pb alloy (32 mol% Li) of 1 g was placed in a MgO tube with a porous bottom and used as a reference electrode. A graphite rod (Tokai Carbon #G347) centered within a MgO shroud was an anode. The stainless steel cathode basket (9 mm in diameter) was surrounded with a 325 stainless steel mesh (sieve openings of 45 μm) to contain 15 g of crushed UO2 pellets sieved into a size range of 0.4 mm to 1 mm.

Characterization.— Agilent E3633A power supply was used for the voltage control electrolysis. The cathode potential was monitored by a digital multimeter (Agilent, 34405A). Autolab 302N potentiostat was used for the cyclic voltammetry. The working electrode of the cathode scans was a Ni wire (1 mmφ). A Pt wire (1 mmφ) and a graphite rod (8 mmφ) were used as working electrodes for the anodic scans. A Pt plate was employed as the counter electrode. The reduction extent was measured with a thermogravimetry (Seiko TG/DTA 6300).

Results and Discussion

Possible cathode and anode reactions and their standard potentials were investigated assuming that the activity coefficients of O2− and CO32− are unity because the solutions are dilute.5 When a C anode is employed, the oxidation reaction is the thermodynamically more favorable CO2 or CO evolution and thus the cell voltage can be decreased by about 1 V compared to the O2 generation (Fig. 1a). It should be noted that CO32− can be formed by the oxidation of O2− at the C anode. In addition, CO2 gas was expected to react with O2− in the molten salt, and to dissolve as CO32−. Thermodynamically stable region of CO32− was evaluated assuming that the activity of CO32− is unity.
is unity. The activity coefficients of $O_2^{-}$ in LiCl and CaCl$_2$ for the correlation of $O_2^{-}$ concentration and activity were 8.4 and 3.9, respectively with pure solid Li$_2$O and CaO as the standard states\textsuperscript{10,11} Unlike the electrochemical reduction in a CaCl$_2$-CaO at 850 $^\circ$C, CO$_3^{2-}$ in a LiCl-Li$_2$O is stable even at very low $O_2^{-}$ concentrations and CO$_2$ partial pressures. Fig. 1b shows that when Li$_2$O concentration is 1 wt% in LiCl at 650 $^\circ$C, the partial pressure of CO$_2$ should be lower than 0.00019 bar for the decomposition of CO$_3^{2-}$\textsuperscript{2}. If CO$_3^{2-}$ is generated, it will transport to a cathode causing contamination of a cathode with C and decrease of current efficiency. CO$_3^{2-}$ formation kinetics in a LiCl-Li$_2$O is unknown. In this study, evolved gases from the anode were swept by Ar gas in the rate of 70 cc/min to decrease the partial pressures of CO$_2$ inside the shroud and prevent the reaction between CO$_2$ and $O_2^{-}$.

In the cyclovoltammogram of a Ni wire before the first run electrolysis (Fig. 2a), a sharp increase of the cathodic current and the corresponding anodic current were observed at around – 0.580 V (vs. Li-Pb), and they were attributed to Li deposition and its dissolution, respectively. In the positive potential region on a Pt wire (Fig. 2b), the gradual increase of the anodic current and the corresponding cathodic current at about 1.754 V (vs. Li-Pb) were observed, and they were attributed to Li$_2$PtO$_3$ formation and its cathodic wave.\textsuperscript{6} A sharp increase of the anodic current in the cyclovoltammogram of a Pt wire before the electrolysis at about 1.974 V (vs. Li-Pb) was attributed to oxygen gas evolution. The measured Li deposition and oxygen gas evolution gave 2.554 V which was close to the theoretical decomposition potential of molten 1 wt.% Li$_2$O in LiCl, 2.551 V. In the case of a graphite rod, the start of gradual increase of anodic current attributed to CO$_x$ gas evolution was observed at 1.015 V (vs. Li-Pb) confirming that anodic evolution of CO$_x$ gas is more thermodynamically favored than that of O$_2$ gas. At present, the rapid rising of the anodic current at about 2.416 V cannot be identified.

Two consecutive constant cell voltage (3.3 V) electrolyses for 340 minutes were carried out for the reduction of UO$_2$ (Fig. 3). The theoretical electric charges necessary for reducing 15 g of UO$_2$ to U metal are 21,441 coulombs. The generated currents were around 2.2 A for the first run with the electric charge that passed through the cell of 44,154 coulombs and 2.0 A for the second run with 41,504 coulombs. During the electrolyses, the cathode potentials were more negative than the Li deposition potential, -0.580 V (vs. Li-Pb). It means that the reduction of UO$_2$ can proceed via the chemical reaction with the in situ generated Li at the cathode basket as we reported.\textsuperscript{10} Interestingly, when the open circuit voltage was measured, the cathode potential became gradually more negative, and was around the Li deposition potential in the last part of the first run suggesting the accumulation of a large amount of Li in the cathode basket. On the other hand, the open circuit voltage of cathode of the second run did not reach the Li deposition potential even in the end of the run implying that there
are still enough oxides to oxidize Li metal. The cross-section view of the cathode basket of the first run gave a metallic gray color of U. However, brown color of UO₂ was still observed from the cathode basket of the second run. The reduction conversion of UO₂ to U was 99% and the current efficiency amounted to 48% for the first run. The reduction conversion and current efficiency were only 57% and 29%, respectively for the second run.

The solidified salt surface after the two consecutive electrolyses showed the generation of C dusts during electrolyses. The insulating MgO anode shroud can prevent the parasite current flow caused by floating C. However, if CO₃²⁻ is generated in the anode, the dissolved CO₃²⁻ can transport to a cathode and easily decompose to C resulting in the decrease of current efficiency as shown in Fig. 1a. The amount of CO₃²⁻ was quantified by the titration using HCl. The measured values for Li₂CO₃ and Li₂O were 0.83 wt% and 0.57 wt%, respectively. 0.83 wt% Li₂CO₃ is equivalent to 0.34 wt% Li₂O. It means that 37% of the O²⁻ reacted with CO₂ or C to form CO₃²⁻ during the consecutive electrolyses. The cyclovoltammogram of a Ni wire after the first run (Fig. 2a) shows the existence of the dissolved ion which was reduced at more positive potentials compared to Li⁺. As we calculated (Fig. 1), it was evidenced that dissolved CO₃²⁻ is inevitably formed in a LiCl-Li₂O molten salt at 650°C unlike a CaCl₂-CaO molten salt at 850°C causing the decrease of reduction yields of metal production.

Conclusions

The electrochemical reduction of UO₂ using a C anode is possible in a LiCl-Li₂O molten salt. However, the inevitably generated CO₃²⁻ caused decrease of the reduction yield and formation of dirty C dusts. The methods to suppress the decomposition of CO₃²⁻ at the cathode such as separation of anode parts by ion-exchange membranes or additional electric circuits to decompose CO₃²⁻ away from the feed material at a cathode should be applied for the use of C anodes in a LiCl-Li₂O molten salt.

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