Study on the Mass Transfer of Oxygen in an Electrolytic Reduction Process of ACP

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1. Introduction

The Advanced Spent Fuel Conditioning Process (ACP) is a molten-salt-based back-end fuel cycle technology developed at KAERI. The target fuel type for the process is the oxide fuel unloaded from PWRs which are the main prototype reactor commercially operating in Korea. The volume and the radiotoxicity of the spent fuel decrease to quarters of the initial volume and radiotoxicity after being reduced to metal forms and removing some elements into a molten salt. The reduction of the two properties improves the convenience in managing the spent fuels and makes it possible for disposal sites to be made the best use of.

Metallization of the spent oxide fuels is accomplished in an electrolytic reduction cell where a molten LiCl is adopted as an electric medium and Li_2O is added to increase the activity of the oxygen ion in the system. A porous magnesia filter, a SUS solid conductor, and the metal oxides to be reduced constitute a cathode and anodes are made of platinum. The only cation in the liquid phase is lithium at the first stage and the ion diffuses through the pores of the magnesia filter and then receives electrons to become a metal. The reduced lithium metal snatches oxygen from the metal oxides in the filter and transforms into lithium oxide which diffuses back to the molten salt phase leaving the reduced metal at the inside of the filter. The lithium oxide is dissociated to lithium and oxygen ions once it dissolves in the molten salt if the concentration is within the solubility limit. Hence the actual diffusing element is oxygen in an ionic state rather than the lithium oxide since there is no concentration gradient for the lithium ion to move on – the lithium ion is the main cation in the system though some alkali and alkaline-earth metals dissolve in the molten salt phase to be cations. The analysis of the mass transfer of oxygen in the electrolytic reduction process is, thus, of importance for the metallization process to be completely interpreted.

2. Mass Transfer Mechanism

The mass transfer mechanism of oxygen could be divided into three steps if the oxygen in the uranium oxide is brought into focus, not in the molten salt phase; 1) internal diffusion from the inside of the metal oxide to the surface of a powder after breaking the interstitial bond between U and O, 2) external diffusion along the surfaces of the powders in the molten salt which is wetting the metal oxide powders, and 3) mass transfer to the bulk liquid phase. The first diffusing step should be considered with the potential changes of various kinds of uranium oxides since the oxidation state of uranium becomes lower as the metallization proceeds [1,2]. The last two steps are very difficult to treat separately. An extraction concept could be applied to the second and the third step together when the cathode – including the magnesia filter and the molten salt dampening the powders – is considered as a porous and homogenous material with a high concentration of the oxygen ion.

3. Mathematical Equations

When a sufficient cathodic potential is imposed on the cathode, the limiting current is expressed as

$$I_l(t) = nFAD_0 \frac{C_0^b(t) - C_0^s}{\delta_0} \approx nFAD_0 \frac{C_0^b(t)}{\delta_0} \quad (1)$$

where A is the cathode area, D_0 is the diffusivity of the interstitial oxygen, and δ_0 is the thickness of the diffusion layer. After a mathematical arrangement, the limiting current is given by

$$I_l(t) = I_l(0) \exp\left(-\frac{D_0 A}{V \delta_0} t\right) \quad (2)$$

The internal diffusion coefficient is, thus, obtained by measuring the limiting current and plotting it with the time.

Osburn and Katz [3] found it necessary to consider the presence of two parallel diffusion processes inside a solid; one faster and one slower. The following equation was developed and applied to the extraction for describing the parallel diffusion.

$$\frac{C_\infty - C}{C_\infty} = \frac{8}{\pi^2}\left[f_1 \exp\left(-\frac{\pi^2 D_1 t}{4L^2}\right) + f_2 \exp\left(-\frac{\pi^2 D_2 t}{4L^2}\right) \right] \quad (3)$$

A plot of the logarithm of the left hand side of Eq.(3) against the time will thus provide the diffusion coefficients of the external diffusion.

4. Experiment

Using an integrated cathode composed of a SUS conductor, U_3O_8 powder, and a magnesia filter, a constant potential is applied between the cathode and Pt anodes. The electrolytic cell is heated by a resistive furnace to be maintained at 650 ^{o}C which is higher than the melting point of LiCl, a medium of the electrolytic cell. Pt reference electrode is adopted by considering its stability in the molten salt at a high temperature. The reactor consists of a twofold crucible system, the inner magnesia and the outer alumina. To determine the external diffusion, the filter was filled with $Li_2O-U_3O_8$ and no potential was applied to make the diffusion occur only by a concentration gradient. The Li_2O added in the filter dissolved in the wetting molten salt and the oxygen ion was formed, which assumed the condition of the external diffusion of the oxygen ion. The concentration change of the oxygen ion diffusing to the molten salt phase was determined by a titration and the rate of the mass transfer was estimated.

5. Results and Conclusions

Fig. 1 shows the current profiles with time and the concentration of Li_2O in the molten salt. The limiting current was irrespective of the concentration of Li_2O even though the initial current of Li_2O 2.5 wt% is greater. The difference at the initial stage reflects the activity of Li_2O and the same value of the limiting current indicates that the internal diffusion of oxygen is the rate-determining step. The external diffusion is plotted and presented in Fig.2. As shown in Fig.2, the external diffusion occurs in parallel – a fast and a slow diffusion.

The mass transfer of the oxygen ion in an electrolytic reduction process was studied in the present work. The oxygen ion diffuses from the inside of the U-O solid solution to the molten salt phase. The diffusion was divided into three steps and the experimental and mathematical approaches were carried out for each step. Although there is a slow diffusion for the external diffusion, it is concluded that the internal diffusion is the rate-determining step of the electrolytic reduction process.
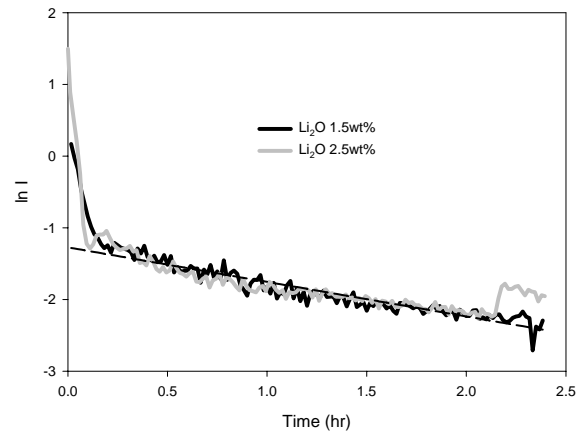

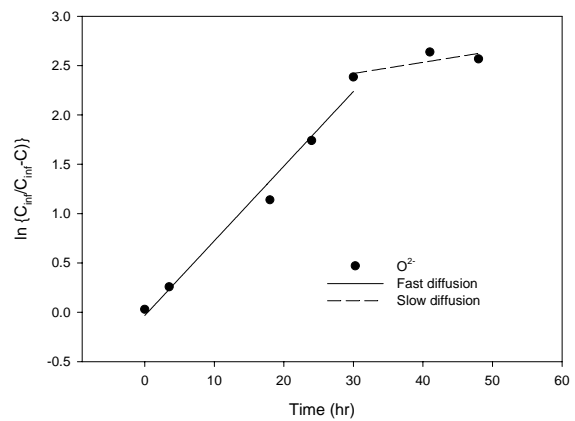Figure 1. Current with time at different Li_2O concentrations in molten LiCl

Figure 2. External diffusions of the oxygen ion

REFERENCES

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