Recovery of Rare Earth and Alkaline Earth Elements by Countercurrent Electromigration in Room Temperature Molten Salts

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Rare earth (RE) and alkaline earth (AE) metals and their compounds are characterized by a variety of physical properties allowing wide applications as functional materials. The wastes like spent catalysts are important secondary sources of RE. Then one must be aware of the importance of the recycle process for the potential secondary sources of RE. Therefore it is necessary to develop the recovery process for RE metal considering from the economic and the environmental reasons for near future. For this purpose, we have already demonstrated the pyrometallurgical process such as the countercurrent electromigration using high-temperature molten salts.[1] Moreover, this dry process does not require a large number of steps compared to the conventional aqueous process. From this point, this process using room temperature molten salts (RTMS) is anxious to have excellent advantages both in safety and in economic aspects.

The TMHA-TfO salt, [n-$C_6H_{13}(CH_3)_3N$][CF_3SO_3] was synthesized by the reaction of [n-$C_6H_{13}(CH_3)_3N$]Br, with $AgCF_3SO_3$. The RE and AE with common anions were reacted with the CF_3SO_3H. Preparation of sample solutions (e.g., $La(TfO)_3$ in TMHA-TfO salt) were carried out to use the electrolyte of the electromigration. The carbon rod and the tungsten wire were chosen as the anode and cathode, respectively. The migration part was packed with the alumina powder with 75 μmϕ. The TMHA and RE ions were analyzed by Ion Chromatography and ICP emission spectrometry, respectively. According to a series of several runs, the result of the salt distribution along the tubes in each fraction was shown in **Fig. 1**. As indicated in Fig. 1, the electromigration method could enrich RE and AE near the anode compared with the initial ratio. As shown in **Fig. 2**, it is efficient to enrich the RE under high current density as the ratio of La in the first fraction was extremely enriched. The quantitative analysis of the internal mobility was carried out as follows.

The relative differences of the internal mobilities, ε, were defined as, $\varepsilon = (b_1 - b_2)/b_{av}$. The ε values can be determined from the chemical analysis and calculated from the following equation based on the material and charge balances derived by Klemm [2].

$$\varepsilon = -(F/Q)(N_1/x_1 - N_2/x_2)$$

The calculated relative differences are tabulated in **Table 1**. It revealed that the RE cations are more immobile than AE expected from the electric valence. Further investigation of the internal mobility for each cation has been estimated from the measurement of the electric conductivity in this RTMS in near future.

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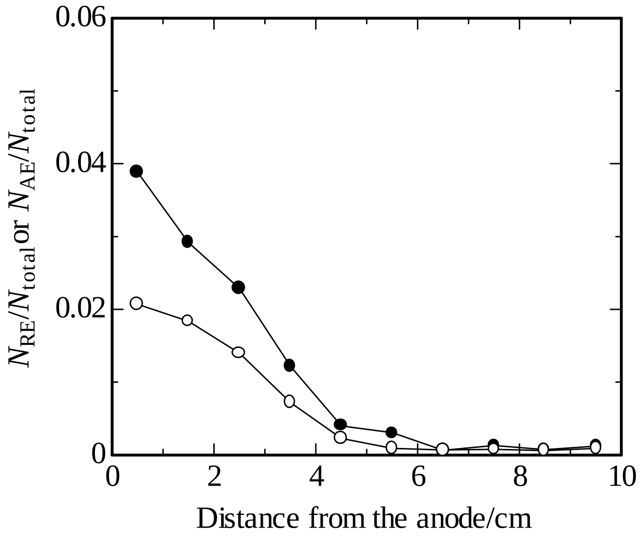

Fig. 1 The concentration profile in the migration tube in the RTMS, TMHA-TfO including $LaTfO_3$ and $BaTfO_2$ at 473K. —●— : N_{La}/N_{total}, —○— : N_{Ba}/N_{total}

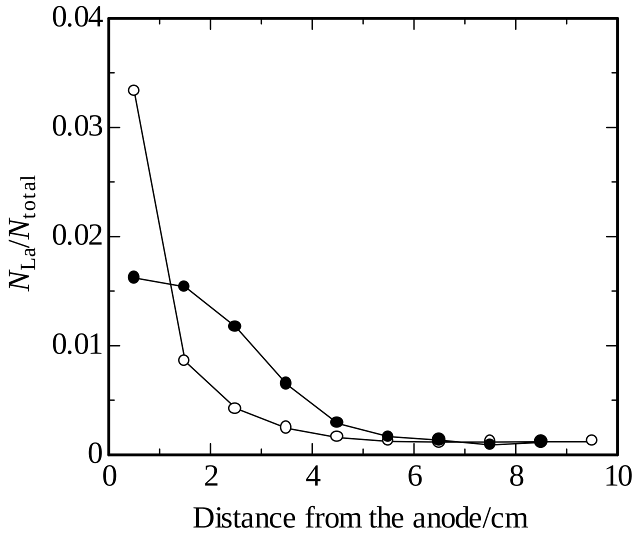

Fig. 2 The concentration profile in the migration tube in the RTMS, TMHA-TfO including $LaTfO_3$ at 473K with the different current densities.
—●— : i_d=0.08Acm^{-2}, —○— : i_d=0.40Acm^{-2}

Table 1 The relative differences for the internal mobilities in RTMS, ($La_{1/3}$, TMHA)TfO, ($Ba_{1/2}$, TMHA)TfO at 473K.

No.	x	Q/C	i_d/Acm^{-2}	ε La	ε Ba
1	0.001	1525	0.08	-0.435	-0.281
2	0.001	1878	0.16	-0.416	-0.212
3	0.001	2505	0.40	-0.627	-0.364
4	0.001	2340	0.24	-0.584	-0.325