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Preparation of a Rare Earth Ion Selective Electrode

Yoshihiro TAKASAKA† and Yasuo SUZUKI*

Department of Industrial Chemistry, Faculty of Engineering, Meiji University, Ikuta, Tama-ku, Kawasaki 214

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Synopsis. A new rare earth-ion selective electrode with a cerium(IV) oxide membrane has been prepared. The electrode was selective for the trivalent rare earths with a slope as great as 58 mV. The electrode was less selective for bi- and quadrivalent cations.

The conventional cation-selective electrodes with solid-state membranes have been prepared from insoluble salts, the iron(III)-selective electrode with a chalcogenide glass membrane[1)] being the only exception. The fluoride-selective electrodes, containing lanthanum fluoride as the membrane, are possibly sensitive to lanthanum(III) ion,[2)] but are of little analytical importance because of a small slope of 20 mV. The solid-membrane electrodes containing either a quadri- or bivalent rare-earth compound are possible sensors for the rare earths(III), with a slope as great as 59 mV. The present work includes the preparation and properties of the cerium(IV) oxide membrane electrodes as rare-earth(III) sensors. Since the trivalent rare earths behave similarly in aqueous solutions, the new electrodes should have identical selectivity for any of the rare earths.

Experimental

All the rare-earth oxides of 99.9% or higher purity were supplied by Shin-etsu Chemical Industries Co., Ltd. The solutions of rare-earth(III) nitrates were prepared by dissolving the respective oxides with nitric acid. Cerium(III) perchlorate and nitrate solutions were prepared from the corresponding salts of I. C. N. Pharmaceuticals Inc. Other reagent solutions were prepared from reagent-grade chemicals.

The electromotive force measurements were performed on a Beckman Model 3500 pH meter with an Orion 90-02 double junction reference electrode. The pH measurements were made by a Denki Kagaku Keiki Model HG-3 pH meter. Electric resistances of the membranes were measured by a Yokokawa Denki Model L-6B insulation-resistance tester.

The appropriate amounts of cerium(IV) oxide and Rapid Araldite, an epoxy adhesive from Ciba-Geigy, were mixed homogeneously, and coated on the copper plate of the electrode body, as shown in Fig. 1. All the electrode behaviors were studied at 25.0°C with an electrode system of: CeO_2 electrode|Solution X|Salt bridge|Ag-AgCl reference electrode.

Results and Discussion

The values of the activity coefficients of the rare-earth ions were selected[3,4)] assuming that the mean activity coefficients of the rare-earth ions do not vary appreciably from ion to ion under identical conditions.

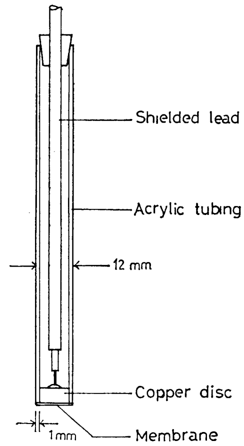

Fig. 1. A cerium(IV) oxide membrane electrode.

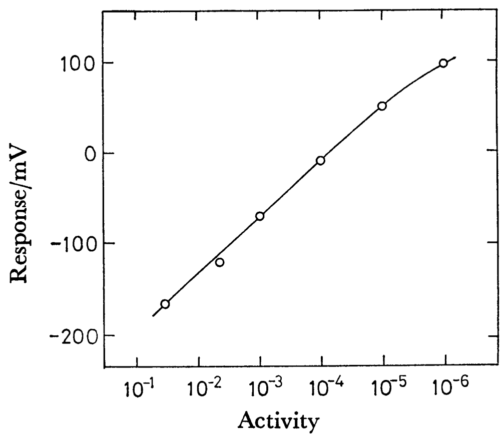

Fig. 2. Response of cerium(IV)-oxide electrode to the cerium(III) activity.

Of the electrodes having membranes of various cerium(IV) oxide concentrations, the ones containing 55% oxide and 45% adhesive in weight exhibited the closest response to the Nernstian theory. The slope of the electrode for cerium(III)-ion concentration ranged from 43 to 58 mV within a concentration range of 10^{-1} to 10^{-6} mol dm^{-3}, while the linear relationship between the response and concentration held only in a range of 10^{-3} to 10^{-5} mol dm^{-3} with a slope of 58 mV. By taking the activity scale, however, the linearity extended from 10^{-1} to 10^{-5}, as shown in Fig. 2. Considering the overall properties studied, the 55-% electrode was found to be superior to the other electrodes of 30—70%, and has thus been used in subsequent work.

The response time of the electrode was determined for several cerium(III) concentrations as 5 to 10 min.

† Present address: Japan Scientific Instrument Co., Ltd., Ichiban-cho, Chiyoda-ku, Tokyo 102.

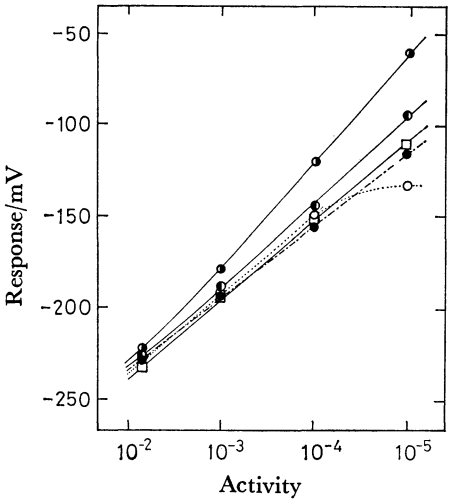

Fig. 3. Response curves of cerium(IV)-oxide electrode for some rare-earth(III) ions.
●: Lanthanum, ○: praseodymium, □: dysprosium, ◐: lutetium, ◑: yttrium.

The effect of the membrane thickness at 55-% cerium(IV) oxide concentration was also examined, and an electrode having a 0.100 g membrane, *i.e.* a 0.13 g cm^{-2} thickness, exhibited the optimum response. The electric resistance of the membrane ranged from 0.2 to 9 MΩ. No appreciable variation in the response behavior was observed within several months of repeated use.

The response behavior of the electrode against five trivalent rare-earth ions, including lanthanum, praseodymium, dysprosium, lutetium, and yttrium, were investigated, and the activity-response relations are shown in Fig. 3. It is remarkable that lanthanum and praseodymium, both adjacent elements to cerium, exhibited lower responses than the heavy rare earths, while yttrium exhibited the highest response among the rare earths examined.

The effect of pH was studied within the pH range of 2 to 9, where it was shown that the electrode could be useful in solutions of pH 3 to 5.5. Both higher hydrogen-ion concentrations and hydroxide precipitation apparently interfere in the measurements in solutions of pH less than 2 and above 6, respectively.

The selectivity coefficients for several cations, determined by separate and mixed solution methods,[5-9] are shown in Table 1. As might be expected, the rare-earth(III) ions exhibited selectivity coefficients as great as unity. Though barium(II) and zirconium(IV) ions did not interfere appreciably, the alkali metals, such as sodium and potassium, did interfere considerably. The latter fact is apparently not desirable when using the electrode in determining stability constants of the rare-earth complexes, where the solutions usually contain appreciable amounts of alkali metal salts, such as potassium nitrate, as the supporting electrolyte.

Though the present results are not sufficient for elucidating the response mechanism, it is probable that the oxidation-reduction reaction of cerium in the membrane and in solution predominates, at least in the case of cerium(III) solutions.

Table 1. Selectivity coefficients for several cations at 10^{-3} M

Cation	Selectivity coefficients	
	Separate solution method	Mixed solution method
Na(I)	1.0×10^{-2}	0.44
K(I)	2.5×10^{-2}	0.10
Ba(II)	0.11	3.5×10^{-3}
Fe(III)	0.20	1.4×10^{-2}
Zr(IV)	—	1.4×10^{-3}
La(III)	1.0	—
Ce(III)	1.0	—
Pr(III)	1.0	—
Dy(III)	1.0	—
Lu(III)	1.0	—
Y(III)	1.0	—

The cerium(IV) oxide-membrane electrode may thus be used as a sensor for the rare-earth(III) ions, with further possible improvements. The current work also includes research on the application of quadri- and bivalent rare-earth compounds as sensing materials, which would account for the response mechanism of the electrodes of the present type.

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