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LANTHANUM FLUORIDE CERAMIC MEMBRANES AS SELECTIVE ELECTRODE FOR FLUORIDE ION

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A new type of fluoride ion-selective ceramic membrane electrode was developed by using lanthanum fluoride, europium fluoride and calcium fluoride. The membrane was prepared by sintering at a temperature higher than 1200°C in an atmosphere of hydrogen fluoride gas stream. Satisfactory response characteristics were obtained over the concentration range of 10^{-1} to 10^{-6}M.

Fluoride ion-selective membrane electrodes have been made either from an europium-doped lanthanum fluoride single-crystal (1) or from slightly soluble fluoride salts embedded in silicon rubber (2). The commercially-available single-crystal membrane electrode has been used for the direct determination over the range of 10^{-1} to 10^{-6}M of fluoride ion activity and also the potentiometric titration was investigated by thorium, lanthanum and calcium salts as the titrants of fluoride with fluoride ion-selective electrode (3). Recent progress on solid-state membrane electrodes encouraged us to investigate ceramic membranes of various polycrystalline mixtures (4), and we are now able to report on a new ceramic membrane electrode with good sensitivity and selectivity for fluoride ions, and to suggest that it should be very useful for analytical purposes.

The membrane was prepared by sintering a mixture of lanthanum fluoride, europium fluoride, and calcium fluoride mixed at the desired amounts at a temperature of more than 1200°C for a time period of 3 to 15 hours in an atmosphere of hydrogen fluoride gas stream. After the membrane had been set in the electrode body, the surface was polished with diamond paste and washed with an ultrasonic cleaner. The electrode contains an internal electrode (silver-silver chloride electrode) immersed in an internal solution for reference (10^{-3}M potassium fluoride and 3M potassium chloride). The potentials developed by the membrane electrode in the test solution were measured with a silver-silver chloride electrode as reference electrode at 25.0± 0.1°C. The response characteristics of these electrode membranes were compared with those of the single-crystal of the fluoride ion-selective electrode made by Orion Research Inc..

The ceramic membrane electrode exhibited about a 59 mV change in potential for each tenfold change in the fluoride ion activity at 25°C and a Nernstian slope was obtained over the concentration range of 10^{-1} to 10^{-5}M. The potential change between 10^{-5} and 10^{-6}M was 56 mV (ASTM method), being considerably better

than the single-crystal electrode. Fluoride ion activity could be determined from 10^{-1} to 10^{-7}M with good accuracy and reproducibility. The electrode potentials were attained rather rapidly, and the equilibrium potentials were read within 40-60 second after immersion of the electrode in the test solution of 10^{-5}M fluoride ion activity. The ceramic membrane electrode was considerably faster in response than the single-crystal one. Effect of co-existence of many other anions on the ceramic membrane electrode could be neglected. For example, adding 0.1 M of chloride ion to a solution containing 10^{-4}M fluoride ion at a constant ionic strength resulted in few decrease in fluoride ion activity. The results similar to those of the single-crystal electrode were obtained in the presence of the complexing agents for lanthanum, such as citrate ion. Iron (III) and aluminum ions interfered with fluoride ion measurements because these ions formed their complexes with fluoride ion. Hydrogen ion also interfered because of the decrease of fluoride activity based on formation of complexes with fluoride in acidic solution below pH 5. The only significant interference on the membrane surface occurred when the concentration of hydroxide about equaled the concentration of fluoride ion, and a tenfold excess of hydroxide would double the apparent fluoride content.

In an attempt to study the effect of incorporation of europium in the electrode membrane, various kinds of ceramic membranes containing lanthanum fluoride alone and mixed with europium fluoride were examined. Ceramic membrane containing lanthanum fluoride alone exhibited unstable and drifting potentials to fluoride ion because of its high resistivity. When europium fluoride was added to lanthanum fluoride, the electrode fabricated from the ceramic membrane thus obtained showed the Nernstian slope to the fluoride ion activity. As for the membrane containing 0.1-0.5 mol % of europium fluoride, the best results were obtained, being in good agreement with that of single-crystal electrode. If the membrane contains more than 1 mol % of europium fluoride, it becomes mechanically weak and less responsive. The results by X-ray diffractometry indicated that the ceramic membrane consisted of a homogeneous solid solution which constituted a single phase, irrespective of its composition of the components, lanthanum fluoride and calcium fluoride. No pores in the ceramic membranes could be observed by a microscope. However, the membranes containing more than 5 mol % of calcium fluoride responded slowly. Continuous potential measurements at 80°C were made using a ceramic and a single-crystal membrane electrodes in a specially designed sample solution circulation cell. The ceramic membrane electrode similar to the single-crystal one was demonstrated to have a very long life time. The lanthanum fluoride ceramic membrane electrode should be available for continuous determinations of fluoride ion activity in public water supplies as well as for many other determinations in water pollution.

References;

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