hydrolysis of OCP under normal conditions, the experiments were carried out at the boiling temperature around 100°C and at a pH of 12. The highest uptake of magnesium by the hydrolytic solid corresponded to 2.08 g atom of magnesium per mol of apatite.

Brown et al. proposed a mechanism for a three dimensional growth of apatite on (100) plane (A-A plane in Fig. 1) which is common for both OCP and HAP structures through an ion rearrangement considered to occur via Eq. (1).

$$\text{Ca}_9\text{H}_2\text{PO}_4\text{OH}_2 + 2\text{Ca}^{2+} = \text{Ca}_9\text{H}_2\text{PO}_4\text{OH}_2 + 4\text{H}^+ + 3\text{H}_2\text{O}$$  (1)

According to Eq. (1), one mol of apatite is formed by the incorporation of two Ca$^{2+}$ ions released in the medium by initial hydrolysis of OCP, into its structure. Since magnesium inhibits the hydrolysis initially, the two Ca$^{2+}$ ions required to form apatite will not be available and we propose that Mg$^{2+}$ ions present in the medium may follow the above sequence of mechanism and the incorporation of two Mg$^{2+}$ ions into HAP may be considered to occur via Eq. (2).

$$\text{Ca}_9\text{H}_2\text{PO}_4\text{OH}_2 + 2\text{Mg}^{2+} = \text{Ca}_9\text{Mg}_2\text{PO}_4\text{OH}_2 + 4\text{H}^+ + 3\text{H}_2\text{O}$$  (2)

If this mechanism were true, calcium and phosphate ions should not be released into the medium and in our experiments practically no calcium and phosphate ions were released during hydrolysis of OCP. Since triangular calcium sites are smaller than the column calcium positions in HAP structure, these places may be the possible loci for magnesium in magnesium containing apatite.

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References


Rectification through Anodic Aluminium Oxide Layers Under Different Metallic Electrodes

R. C. Saini, R. K. Nigam* & Kuldeep S. Dhindsa

Central Quality Testing Laboratory, Department of Chemistry & Biochemistry, Haryana Agricultural University, Hisar 125004

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Rectification studies through the anodic aluminium oxide films on super-purity aluminium have been carried out using vacuum-deposited metals, viz. Cu, Ni, Cd, Pb, Sn and Al as counter electrodes. Both symmetrical and unsymmetrical current-voltage characteristics are shown by the films of different thicknesses under Al and of same thickness under different metals, as counter electrodes. Surface property and flaw density of the film are responsible for rectification phenomenon through anodic oxide layers.

MUCH work in recent years has been carried out on electrolytic faradic rectification but only a little effort has been made to investigate rectification phenomenon using M/M$_2$O$_y$/M' sandwich, especially in the case of anodic oxide films on aluminium. The continuity of these films has been recently established. The aim of the present investigation is to study the mechanism of rectification through these films using different vacuum-evaporated metallic counter electrodes and to examine the correlation between critical voltage and work function of the counter electrodes, if any.

Aluminium specimens were cleaned, polished and encapsulated as described earlier. The encapsulated specimen was anodized under constant current conditions in non-aqueous glycol-borate electrolyte at 25°C and current density = 1.0 mA/cm$^2$. First set consisted of 90V films with evaporated Cd, Cu, Ni, Pb, Sn, and Al whereas the second set of 30, 50, 80, 110 and 150V films with Al metal as counter electrode. The metallic contact with oxide films was made by evaporating the metals under high vacuum (≈10$^{-4}$ torr). D.C microvoltmeter (Philips model PP-9004) and a regulated power supply, 0 to 10V, which could read up to ±0.1V, were em-
ployed for this investigation. Throughout this study a ten megohm resistance was kept in series with the specimen. The sample was kept in an automatic air-circulating oven at 40°. The current-voltage behaviour of aluminium oxide films under different electrodes with respect to zero bias, was both symmetrical and unsymmetrical. The symmetry of the films depended markedly upon the nature of counter electrode, with lesser contribution by oxide film thickness. A hundred-fold increase in the current was observed on the application of d.c. bias in the range 0 to 6V across the oxide film. The current-voltage characteristics of first set at lower voltage, i.e., 0 to 1V, exhibited the phenomenon of breakdown similar to the typical back-diode static characteristics. The current through Cd and Sn specimen increased by an order of ten up to 5.1 and 35V, respectively. Cadmium specimen showed further ten-fold rise in magnitude of current at 5.2V beyond which a continuous sparking was observed. For Sn specimen, at the stage of 35V, sparking was observed at the surface of the film but the specimen still retained its asymmetric conduction characteristics even after a sparking. For all the specimens, except Ni, forward critical voltage was nearly independent of the nature of counter electrode, whereas the reverse was not true. This could be substantiated by the fact that the thermionic work function for these metals varied from 4.0 to 4.5eV. The work function potential depends upon the density of states in the conduction band of the metal in contact with the insulating aluminium oxide film. An increase in the critical voltage, the voltage after which the current showed an abrupt rise in current, in the range 2 to 6V, with increasing film thickness was observed in the present study. This showed a direct relationship between flaw density and oxide thickness. A slight variation in the magnitude of critical voltage for both forward and backward directions for a given thickness could be attributed to the surface state of bulk Al (experimental sample) and thin Al (vacuum-evaporated) metal.

It appears that both factors i.e., the thermionic work function of metal electrode and the presence of electrons and weak-spots ‘flaws’ in particular, contribute towards rectification through the oxide films under the influence of applied field. Mechanistically, the applied voltage across an anodic oxide film on aluminium specimen activates the free current carriers—electrons and flaws or voids—inside the films. Some of these current carriers attain a sufficiently high energy under the field applied and then on arriving at the surface of the film overcome the work function barrier of the counter electrode, and get emitted from the solid suddenly. These current carriers are responsible for the rectification characteristic through the anodic oxide films.

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References


Determination of Standard Potentials of Copper-Copper Pyrophosphate & Nickel-Nickel Pyrophosphate Electrodes

M. P. Singh† & Wahid U. Malik‡
Department of Chemistry, University of Roorkee, Roorkee

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Copper-copper and nickel-nickel electrodes reversible to pyrophosphate ions have been prepared and their standard potentials determined. The values of the standard electrode potentials (E°) found are: -0.358 V and -0.388 V respectively. The e.m.f. values of the metal-metal pyrophosphate cells, set up with and without transport, are also reported.

Earlier, we have reported cobalt-cobalt electrode which is reversible with respect to pyrophosphate ions. In continuation of this work, we report now the preparation of metal-metal pyrophosphate electrodes [where metal is copper(II) or nickel(II)], the e.m.f. values of the metal-metal pyrophosphate cells with and without transport as well as the potentials of the two electrode systems. The experimental arrangements were similar to those reported by Poarce and Ough with some minor modifications.

All the reagents employed were of AR grade (BDH) except pyrophosphoric acid and sodium pyrophosphate which were E. Merck products. All the solutions were made in doubly distilled water. Mercury, used for preparing the amalgam and mercuric chloride, was triply distilled.

Preparation of the complex — Solutions of cupric chloride (nickel nitrate in the case of nickel complex) and pyrophosphoric acid (conc. 1.0 M each) were mixed in 1:2 molar ratio. These mixtures were concentrated by heating on a water-bath. On cooling, the precipitates settled down; these were filtered, washed several times with water and then dried at 90°C. The sodium amalgam electrode was prepared as described in the literature.

Metal electrode — A thin film of metal (copper or nickel) was deposited on a platinum foil (area 1 sq. cm) by the electrolysis of a solution containing copper/nickel sulphate (56%), boric acid (3%) and...