Communication

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Growth of Zn²⁺ conductive hopeite

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Ionic Conduction in Zn$_3$(PO$_4$)$_2$·4H$_2$O Enables Efficient Discharge of the Zinc Anode in Serum

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In 1866, Georges Leclanchè introduced the Zn|NH$_4$Cl$_{aq}$|MnO$_2$/C battery. Ever since, more Zn anodes batteries have been produced than all other batteries combined. In its dry version, with porous NH$_4$Cl$_{aq}$-soaked paper between the electrodes, the battery was paper-packaged. Because the Zn reacted non-faradaically with dissolved O$_2$, the shelf life was short and the Zn utilization efficiency was poor. To lower the corrosion potential and corrosion rate, the NH$_4$Cl$_{aq}$ was replaced by KOH$_{aq}$, the electrolyte used now in all Zn anode batteries. The alkaline cells required a steel case, which had limited their miniaturization. As the volume of their electroactive ingredients decreased, the volume fraction of their case increased. Today the smallest batteries are about 10 mm^3. A 100-fold smaller battery could power a miniature, case-less, weekly user-replaced autonomous transponder-interrogated monitor in the human body, such as a continuous amperometric glucose monitor for the management of diabetes.[1]

Here we show that the corrosion of Nafion-coated zinc anodes is drastically reduced at neutral pH both in aerated physiological saline buffer solution (pH 7.4, 0.15 M NaCl, 20 mM phosphate) and also in serum when overgrown by large nonporous lamellae of hopeite [Zn$_3$(PO$_4$)$_2$·4H$_2$O] (Figure 1). Like other inorganic crystals, the nonporous hopeite lamellae are impermeable to O$_2$. Blockage of O$_2$ transport leads usually to simultaneous blockage of ion transport, which requires pores and therefore prohibits the operation of noncorroding anodes. We have found, however, that hopeite is an ambient temperature solid electrolyte, allowing 86% efficient discharge of Zn fiber anodes in the physiological saline buffer, even at a slow, 3-week, rate. The cell Zn|serum|Ag/AgCl, made with a fine Zn fiber anode, also operates at 1.00 V and 13 μA cm^{-2} for 2 weeks, at 60% current efficiency.

The anodes were prepared by electroplating a 20-μm-thick Zn layer on 2-cm long, 76-μm-diameter platinum wires at 2 mA constant current, in 1000 seconds, from 0.6 M ZnCl$_2$, 2.8 M KCl, 0.32 M H$_3$BO$_3$, with 0.3% polystyrene sulfonate, 2 coulombs being passed. Their initial surface area was 0.075 cm^2. The anodes were coated with a 16-μm-thick Nafion film by dipping in 0.5% (10:1 2-propanol diluted) 5% Nafion and drying. Cells of 1.02 ± 0.01 V open-circuit voltage were formed with Ag/AgCl cathodes. The cathodes were much larger than the anodes, making the cell characteristics anode-controlled. To test the cells under conditions of high corrosive loss of anodic capacity, the cells were discharged slowly, at 1 μA (13 μA cm^{-2}), across a 1 MΩ resistor at about 1 V.

When the Nafion-coated Zn anode was discharged in the physiological saline buffer, it was overgrown by colorless crystals and the diameter of the anode increased from 152 μm (Pt wire, 76 μm; Nafion 2 × 16 μm; Zn 2 × 20 μm) to 485 μm at completion of the discharge. The X-ray powder diffraction pattern of the crystals overgrowing the Nafion was identical with that of Zn$_3$(PO$_4$)$_2$·4H$_2$O (Aldrich, Milwaukee, WI) and agreed with the data on PDF card
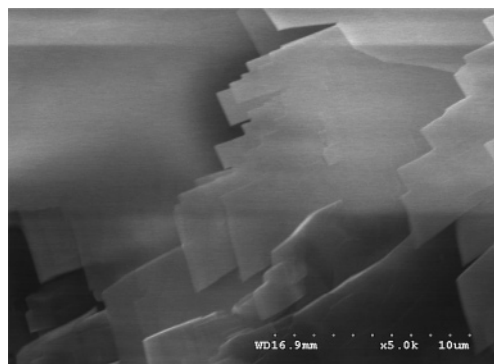
Figure 1. Hopeite Zn$_3$(PO$_4$)$_2$·4H$_2$O lamellae overgrowing the Nafion-coated zinc fiber anode upon its discharge in pH 7.4 physiological (20 mM phosphate, 0.15 M NaCl) buffer. 5000× electron micrograph.
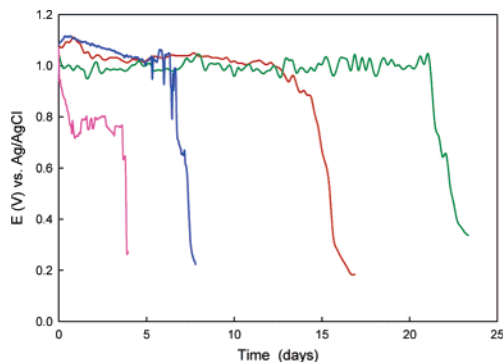

Figure 2. Time dependence of the potential of the Zn anode. The anode was discharged against an Ag/AgCl cathode at a constant current of 1 μA at 25 °C in aerated serum (red), in pH 7.4, 0.15 M NaCl and 20 mM phosphate buffer (green), in 0.15 M NaCl (blue), and in pH 7.4, 20 mM phosphate buffer, without NaCl (magenta).

no. 33-1474 for hopeite (International Centre for Diffraction Data, 12 Campus Blvd., Newton Square, PA 19073) and with those reported for synthetic hopeite.[2] The nonporous lamellar microstructure of the film formed is shown in Figure 1.

Figure 2 (green trace) shows the discharge curve at 1 μA for the cell with physiological saline buffer as its electrolyte. Figure 2 (red trace) shows the curve for the cell with serum. With serum, the output, near 1 V, was steady for two weeks, during which the charge passed was 1.2 C, corresponding to 60% efficiency of utilization of the 2 C consumed in forming the Zn plate. In the physiological buffer, the output, also of 1 V, was steady at for three weeks, and the charge passed was 1.73 C, corresponding to 86% Zn utilization.

Growth of the nonporous lamellae and high anode utilization efficiency required Nafion, phosphate, and NaCl. Without phosphate (Figure 2, blue trace) the hopeite film could not form. In the absence of NaCl, the crystals overgrowing the electrode were not large hopeite lamellae, but were small and columnar, (Figure 2, magenta
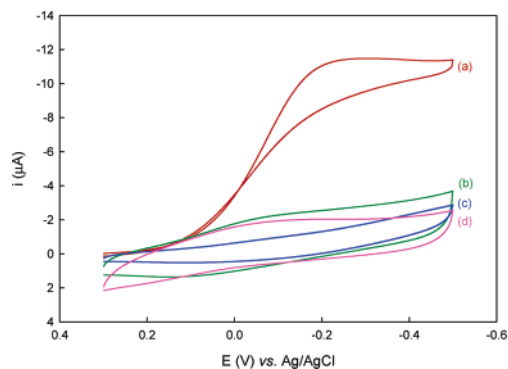
Figure 3. Cyclic voltammograms showing the blockage of O_2 transport to the Zn anodes. The 0.075 cm^2 anodes are Nafion-coated and 2 cm long. The voltammograms are for a set of anodes, differing in their amount of electrodeposited Zn, i.e., (a) 0.00 C, (b) 0.05 C, (c) 0.12 C, and (d) 0.20 C, after completion of their discharge and were obtained in air-equilibrated pH 7.4, 0.15 M NaCl and 20 mM phosphate buffer.

Table 1. Dependence of the Polarization on the State of Discharge of the Zn Anode[a]

J	0%	10%	25%	50%
0.013	0.01	0.00	0.01	0.01
0.026	0.01	0.00	0.01	0.02
0.065	0.02	0.00	0.04	0.04
0.13	0.04	0.01	0.08	0.09
0.26	0.05	0.06	0.19	0.16

[a] J in mA cm^{-2}; after discharge at 13 μA cm^{-2}; all values in V ($\pm$0.01 V).

trace). In the absence of Nafion, the nucleation of the growing hopeite was inhomogeneous and the electrode was not uniformly protected against corrosion.

At the physiological pH of 7.4, the dominant non-faradaic reaction of Zn is that with dissolved O_2.[3] The extent to which the flux of O_2 to the surface of the operating anode is reduced defines the current efficiency. That the high anode utilization efficiency resulted from blockage of permeation of O_2 to the active Zn by the hopeite film was confirmed as follows. A set of anodes was prepared by electrodepositing different amounts of Zn on the Pt wires. Upon completion of their discharge, their cyclic voltammograms were measured, the potential scanned to -0.5 V vs Ag/AgCl, where O_2 is electroreduced even on noncatalytic conductors (Figure 3). The voltammograms confirmed that the hopeite film blocked the O_2 permeation. To establish that O_2 corrosion is prevented even by a very thin hopeite film, the electrodes were discharged to about 0.1% depth and then were kept resting in the aeraeted physiological buffer for two weeks. The thin-film-protected anodes retained 70% of their maximal Coulombic efficiency, proving that thin films are protective and that the anode operation is interruptible.

O_2 transport-blocking films are rarely solid electrolytes and are usually highly resistive to passage of ionic currents. Thus, with few exceptions, anodes with O_2 transport-blocking films discharge only at high overpotentials. The nonporous lamellar hopeite-overgrown Zn anodes were, nevertheless, discharged with little polarization, even when their overgrowth was 100 μm thick. Measurement of the polarization of a set of identical Zn anodes after their discharge to 0, 10, 25, and 50% depth in the physiological saline buffer solution (Table 1) showed that, at a current density of 0.13 mA cm^{-2}, the polarization of the half-discharged anodes differed by <50 mV from their polarization at the start of discharge. At 0.26 mA cm^{-2}, the polarization of the half-discharged anodes exceeded their initial polarization by only about 110 mV, from which we estimate that the ionic conductance exceeded 2 × 10^{-3} S.
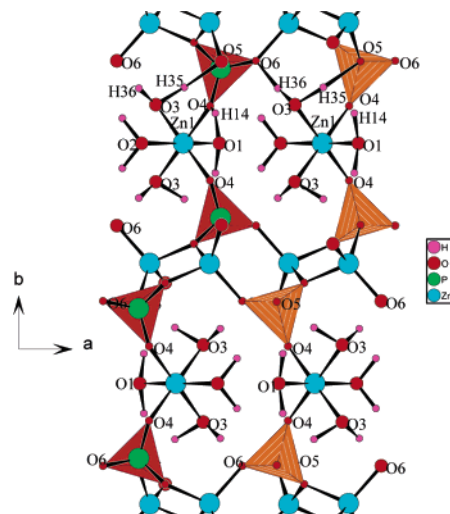

Figure 4. Structure of hopeite $Zn_3(PO_4)_2 \cdot 4H_2O$. Water channels in which Zn^{2+} can diffuse are seen. Selected hydrogen bonds are shown: H14−O4, H35−O5, and H36−O6 (after Whitaker[4]).

Hopeite, an open-framework hydrated zinc phosphate with intersecting channels, is a known host of neutral organic molecules and cations, resembling in this aspect zeolites. The overgrowth of the Nafion-coated zinc anode by hopeite lamellae continues throughout the entire discharge period, their size reaching about 20 μm × 20 μm × 1 μm (Figure 1). The continued growth, as long as the supply of Zn^{2+} lasts, implies permeation of either phosphate and water or Zn^{2+}. The hopeite crystal[4,5] consists of layers of ZnO_4 tetrahedra, linked by PO_4 groupings (Figure 4). Between these two sheets, a crystallographically separate Zn atom, Zn1 (Figure 4), is present in octahedrally coordinated units of $ZnO_2(H_2O)_4$. Two oxygen atoms are shared with two separate PO_4 tetrahedra. The four water molecules form a hydrogen-bonded network. This Zn^{2+} atom site contains vacancies,[6] is replaceable by Ni^{2+} [7] and by Co^{2+},[8,9] and is exchanged by Li^+ or Cs^+, suggesting that the lattice-permeating ion is Zn^{2+}.

In combination with the Ag/AgCl cathode, the hopeite-overgrown zinc fiber anode forms an interruptible cell, operating at 13 μA cm^{-2} at 1 V at a zinc utilization efficiency of 86%. With a chlorided silver fiber cathode, overcoated with cross-linked hydrated poly-(ethylene oxide) or with another bioinert chloride-permeable hydrogel,[10] the anode could form a miniature *in vivo* cell about 100-fold smaller than the smallest available battery and could operate for about two weeks.

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