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9. Hubert *et al.* (*8*) estimate the minimum size of the perennial lake as 2160 km^2 and the maximum size as possibly greater than 5000 km^2. The minimum central depth is estimated to have exceeded 20 m and might have exceeded 80 m. Throughout this report the track-maker is described as swimming, although in the hypothesized restoration the dinosaur's feet necessarily touch bottom and the animal is arguably "wading," and not in the strictest definition "swimming." It is certain that all or nearly all the animal's mass was buoyed up by water, so the animal was at least floating. Also, sequences of footprints begin and end abruptly, and there are several single prints that are isolated within a large surface obviously suitable for the preservation of tracks. Unless these were made by a deus ex machina, the track-maker must have been truly swimming at times. The estimate of water depth at the time the tracks were made is based on the assumption that the proportions and posture given in the restoration (Fig. 3) are approximately correct, with a suggested hip height of about 2 m. However, there is always the possibility that the animal was completely submerged, and pushing along the bottom hippo-style, in which case the water depth would have been considerably greater.
10. J. F. Hubert, personal communication.
11. An exact determination of the dinosaur's size is not possible. Under the hypothesized mode of track formation the width of each footprint is less than normal and the stride length is probably abnormally long. Moreover, stride length is notoriously unreliable for calculating the size of a track-maker because the parameter varies over a wide range of values depending on the animal's speed. If the proportions of the restored animal are approximately correct (Fig. 3), a total length of 6 to 7 m is estimated.
12. R. S. Lull, *Conn. State Geol. Nat. Hist. Surv. Bull. 81* (1953), p. 1.
13. Some prosauropods, especially *Plateosaurus*, are large enough to have made *Eubrontes* prints, but these animals have a peculiar entaxonic tetradactyl foot that has long been associated with *Otozoum*-form footprints.
14. Bipedal dinosaurs may have one of three major ungual patterns: (i) sharply pointed, laterally compressed, or nearly circular, strongly hooked true claws; (ii) pointed, dorsoventrally compressed, flat-bottomed, narrow semiclaws; and (iii) broadly rounded, dorsoventrally flattened hooves. Among Jurassic dinosaurs, only stegosaurs combine true hooves with a tridactyl pes. Most pre-Cretaceous ornithopods have semiclaws. True claws, found only in the Theropoda, can be recognized in footprints by their tendency to form an isolated, nearly circular pit just anterior to the distalmost interphalangeal pad. Semiclaws lie flatter against the substrate, leaving an elongate, sharply pointed triangle at the end of each toe. *Eubrontes* prints have a diversity in the shape of the ungual imprints, and on this feature alone such prints could not be identified with certainty as theropod rather than ornithopod.
15. P. M. Galton, *J. Paleontol.* **45**, 781 (1971).
16. Amherst College contributed toward the preparation of this report.

10 July 1979; revised 30 November 1979

Oxygen Ion–Conducting Ceramics: A New Application in High-Temperature–High-Pressure *p*H Sensors

Abstract. *Membrane electrodes fabricated from yttria-stabilized zirconia, a representative oxygen ion-conducting ceramic, show a linear voltage response to* pH *over the range 3 to 8 at 285°C and a pressure of 1200 pounds per square inch (82 atmospheres). Test units have been operated continuously at 285°C without failure for periods as long as 9 days. Unlike sensors which are based on electron transfer couples, such membrane electrodes are insensitive to changes in the oxidation-reduction environment and, in turn, exert no influence upon the environment. Such ceramic membranes can therefore be used for the direct measurement of the* pH *of geothermal brines, of water in nuclear reactors, and in high-temperature thermodynamic studies on aqueous systems.*

There has long been a recognized need for a stable sensor for measuring the *p*H of high-temperature solutions such as geothermal brines, water in nuclear reactors, and in high-temperature thermodynamic studies on aqueous systems (*1*). In response to this need, attempts have been made to develop suitable sensors based upon the palladium hydride electrode (*2*), the glass electrode (*3*), and metal-metal oxide couples (*4*). Quite surprisingly, no effort appears to have been directed toward the application of oxygen ion-conducting ceramic membranes for this purpose in spite of certain parallels to well-known inorganic ion-specific sensors such as the lanthanum fluoride electrode for fluoride ion (*5*) and the extensive electrochemical studies of stabilized zirconia ceramics in connection with high-temperature fuel cells (*6*) and oxygen sensors (*7*).

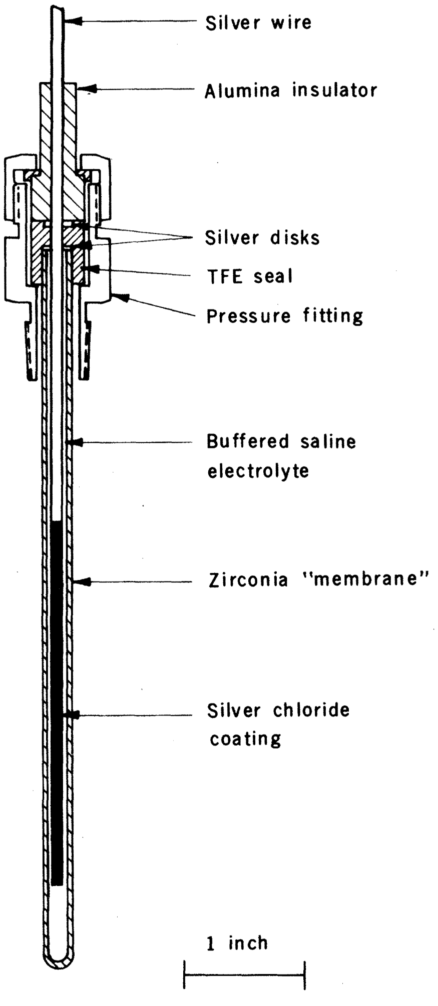

Fig. 1. Schematic diagram of the sensor; *TFE*, Teflon.

I have recently discovered that such oxygen ion conductors, as exemplified by yttria-doped zirconia, show excellent response to *p*H when incorporated into structures reminiscent of the conventional glass electrode. In this form they apparently function as typical membranes with the oxygen ion serving as both the current carrier and the potential-determining species in equilibrium with the hydrogen ion in the aqueous phase. In the work reported here, yttria-stabilized zirconia tubes of the type used in fuel cells and oxygen sensors were prepared by conventional slip casting and plasma spraying techniques (*8*). The tubes [6 inches long and 0.25 inch in inside diameter with a wall thickness of 1/32 inch (1 inch = 2.54 cm)] were stabilized with 8.0 and 16.9 percent yttria (by weight).

The first indication that the ceramic membranes could function as *p*H sensors was obtained from experiments performed at ambient temperature in which zirconia tubes containing 0.1*m* NaCl buffered to *p*H 7.0 as an internal electrolyte were used. An insulated, chlorided silver wire served as the internal electrode, and measurements were made against the reference arm of an Ingold combination electrode as the system was equilibrated with solutions of different *p*H including 0.1*m* HCl, 0.1*m* NaOH, and phosphate buffers. From comparisons of the response to that of the Ingold glass electrode, I found that the behavior of the zirconia membrane as a *p*H sensor was excellent. Because of its high impedance ($> 10^{11}$ ohms at 25°C), however, the sig-

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nals at ambient temperature were "noisy" and measurements had to be made with a high-impedance electrometer (Keithley model 602) in a faraday cage. Such noise was not a problem in later measurements at elevated temperatures because the membrane impedance falls rapidly as the temperature is raised.

For the measurements at 285°C (representative of nuclear reactor water), the structure shown in Fig. 1 was used. As at the lower temperature, a buffered saline inner electrolyte was used in conjunction with the chlorided silver wire. In this case, however, it was necessary to seal the open end of the zirconia tube to maintain the pressure. This was accomplished with a Teflon cap that was compressed within a Conax pressure fitting (Fig. 1). This unit was then mounted in the lid of a 1-liter, 316 stainless steel or titanium autoclave that also held an insulated platinized-platinum wire and a reference electrode. The reference electrode consisted of a chlorided silver wire immersed in a 0.01*m* KCl solution contained within an insulating tube; communication with the water in the autoclave was accomplished through a porous junction (*9*).

With the test system, it was possible to pump water, acid, or base into the heated and pressurized autoclave. This permitted slow changes in *p*H by "titration" with dilute acid (0.0005*m* H_2SO_4) or base (0.001*m* NaOH) or rapid changes by the introduction of aliquots of more concentrated reagent.

Since a well-established comparison standard (like the commercial glass electrode used in the measurements at ambient temperature) is not available for 285°C, the response of the membrane was compared to that of an "oxygen electrode" formed by the platinized-platinum wire in contact with the reagents that were all saturated with air at ambient temperature before entering the autoclave. Under these conditions of constant oxygen concentration, the oxygen electrode can serve as a *p*H sensor because hydrogen ions participate in the potential determining reaction

$$O_2 + 4\,H^+ + 4\,e^- = 2H_2O$$

Although not rigorously established as a *p*H sensor, the response of the oxygen electrode to *p*H has been demonstrated at ambient temperature (*10*), and it should behave more reversibly at the elevated temperature.

The data in Fig. 2, obtained with a membrane stabilized with 16.9 percent (by weight) yttria, show excellent linear correlation between the membrane sensor and the oxygen electrode over a range of *p*H. Additional data illustrating the parallel responses of the membrane electrode and the oxygen electrode to relatively rapid changes of *p*H at 285°C are shown in the inset to Fig. 2. These transitions were accomplished by introducing aliquots of 0.1*m* NaOH and 0.05*m* H_2SO_4 into the feed stream to the autoclave. The rate of response in these experiments therefore reflects the transport rate of the added base or acid through the lines rather than the response time of the sensor itself.

The responses of membrane and oxygen electrodes were also compared with the theoretical value calculated for the transition between 0.0005*m* H_2SO_4 and 0.001*m* NaOH from available thermal data. Were H_2SO_4 a typical "strong" acid at both 25° and 285°C, the *p*H of a 0.0005*m* solution would be ~ 3.0 at both temperatures. Actually, the second ionization constant falls from 1.2×10^{-2} at 25°C to about 3.3×10^{-6} at 285°C (*11*). As a result, the second ionization is almost completely suppressed at elevated temperatures, and the *p*H of a 0.0005*m* solution at 285°C is about 3.3. In the case of 0.001*m* NaOH, the *p*H at 285°C is about 8.2 rather than 11 as at 25°C because of the increased dissociation constant of water at the elevated temperature. From these calculated *p*H values and the theoretical RT/F slope (where R is the gas constant, T is the absolute temperature, and F is the faraday) of 110.8 mV per *p*H unit, a total response of 543 mV is expected for both the oxygen electrode and the membrane at 285°C.

The comparisons were made for five different sensors in tests extending over some 6 months. The same equipment was used throughout, but the platinized-platinum and reference electrodes were replaced occasionally. In the first test, in which relatively new equipment was used, the responses of the sensor and the oxygen electrode were 66.3 and 69.3 percent of theoretical, respectively. In successive tests, agreement with theory improved until it leveled off at approximately 94.0 and 98.6 percent of theoretical for the sensor and oxygen electrode response. Throughout the period, the response of the membrane sensors was 95.3 percent of that of the oxygen electrode (with a standard deviation of 3.8 percent), and no trend with time was evident.

I believe that the initial large dis-

Fig. 2. Correlation between the cell potential *E* of the membrane sensor and that of an oxygen electrode (run ZR02-7, tube Y_2O_3-8, 285°C). Points obtained with 0.0005*m* H_2SO_4 and 0.001*m* NaOH are identified; others were obtained with air-equilibrated water and water to which increments of base were added. The inset shows the response to injections of 0.1*m* NaOH and 0.05*m* H_2SO_4 (run ZR02-6, tube Y-9, 285°C).

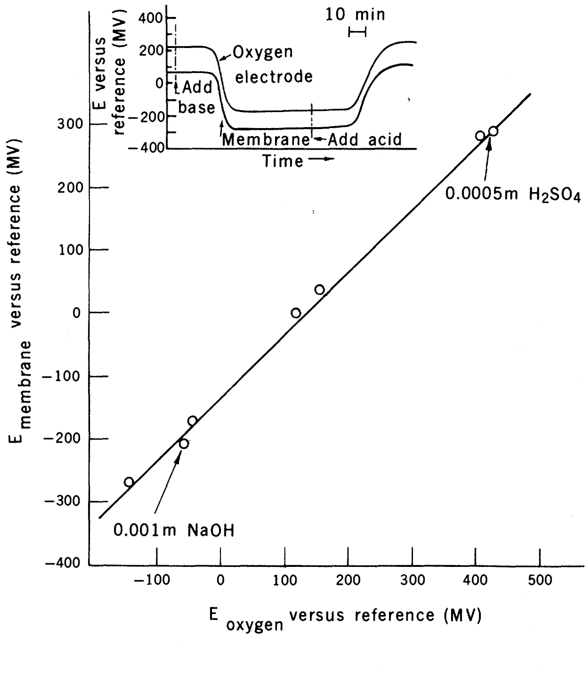
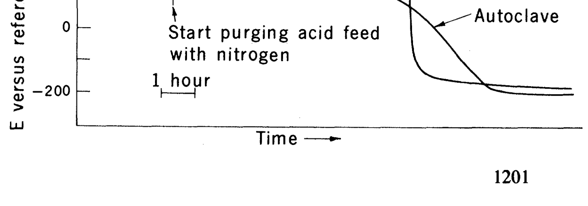


Fig. 3. Behavior of the membrane sensor as the oxidation-reduction potential of the environment is changed (run ZR02-5, tube Y-7, 285°C).



crepancies reflected a significant deviation in the actual *p*H changes from theory because of consumption of acid by corrosion of the walls of the relatively new equipment. During the course of several months of operation the equipment passivated sufficiently that corrosion became minimal, and excellent agreement between theory and experiment was finally obtained. The small residual differences at the end of the test period probably continue to reflect small losses of acid through corrosion, some shunting of the membrane path, and some variation in the junction potential of the reference electrode with the solution in the autoclave.

An additional aspect of the membrane electrode that was examined was its stability in the presence of changes in the oxidation-reduction potential of the environment. This is one of the very real theoretical advantages of a membrane type *p*H sensor over sensors whose response is based on electron transfer reactions. The effect is illustrated in Fig. 3. (Also included in Fig. 3 is the potential of the autoclave wall which was monitored against the reference electrode.) It is seen that, after changing from an air to a nitrogen purge of the incoming $0.0005m$ H_2SO_4, a slow downward drift in potential is evident for the platinum electrode and the wall of the autoclave. This is associated with simple dilution of the oxygen concentration in the water within the autoclave. After several hours a more rapid drop in both these potentials occurred. This is attributed to loss of the passive film on the autoclave with an associated increase in corrosion rate to liberate hydrogen. The platinum electrode then clearly shows its sensitivity to this change in the oxidation-reduction environment. The zirconia membrane electrode, however, retained an essentially constant potential throughout the transients; that is, it is insensitive to changes in the oxidation-reduction potential of the environment, as expected from theory. The small transient in potential at the time of the depassivation is believed to be a response to a real change in *p*H.

This work demonstrates that it is possible to use an oxygen ion–conducting ceramic in a membrane type *p*H sensor. I believe that the structure can be developed into a device for reliable, practical measurements of *p*H at high temperatures and pressures.

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Phenolic Ethers in the Organic Polymer of the Murchison Meteorite

Abstract. *Seven phenolic acids and many nonphenolic organic acids, including large amounts of meta-hydroxy (3-hydroxy) benzoic acid and 3-hydroxy-1,5-benzenedicarboxylic acid, were obtained from the organic polymer of the Murchison C2 chondrite upon oxidation with alkaline cupric oxide. The phenolic acids apparently were derived from phenolic ethers in the polymer, which in turn probably were formed from carbon monoxide and hydrogen by catalytic Fischer-Tropsch type reactions in the solar nebula. In contrast, terrestrial polymers such as lignin, humic acid, and coal yield mainly para-hydroxy (4-hydroxy) benzene derivatives by the same oxidation procedure.*

Most of the organic matter in carbonaceous meteorites (70 to 95 percent) is present as an ill-defined, insoluble macromolecular material, usually referred to as organic polymer (*1–4*). In some respects it resembles polymeric terrestrial organic matter, such as soil humic acid and coal, but its structural units have been only partially characterized (*2–4*). Recently, we have identified 15 aromatic ring systems as the corresponding carboxylic acids, upon oxidation of the Murchison polymer by aqueous $Na_2Cr_2O_7$ (*4*). This oxidation preferentially attacks aliphatic and alicyclic methylene linkages with minimum degradation of most aromatic ring systems except phenols and some heterocyclics (*5*). We now report a similar study in which we used alkaline CuO. It is a mild oxidant specific for cleaving ether linkages without destruction of phenolic rings but is not very effective for oxidizing methylene chains (*6–8*).

To remove soluble organic compounds and possible terrestrial contaminants, 36 g of finely powdered Murchison meteorite (*9*) was extracted successively with $5N$ HCl (refluxed for 24 hours), $0.5N$ NaOH (room temperature for 24 hours), and benezene-methanol (3:1, refluxed for 24 hours) before oxidation. The resulting residue (48.6 percent of the original sample weight) contains 4.1 percent carbon (*10*). An 11.5-g sample of the residue was oxidized with alkaline CuO (10.5 g of $CuSO_4 \cdot 5H_2O$, 8 g of NaOH, and 40 ml of water) at 200°C for 8 hours by the method described in (*6*). After separation of the insoluble residue, the alkaline solution was acidified with HCl, concentrated, and extracted repeatedly with benzene-ether (1:3) and finally with methanol. An alkali-soluble, solvent-insoluble fraction was recovered from the aqueous phase. The methanol extract (196 mg) and the alkali-soluble fraction (183 mg) were found by gel permeation chromatography and solid-probe mass spectrometry (*11*) to consist essentially of humic acid-like material (*12*). The benzene-ether extract (organic acids, 82 mg) was derivatized with d_6-dimethyl sulfate to yield d_3-methyl-labeled derivatives, which were analyzed by gas chromatography–mass spectrometry (GC-MS), solid-probe MS, and high-resolution MS (*13*). The results are shown in Fig. 1 and Table 1.

Of particular interest is the high abundance of *m*-hydroxybenzoic acid (**I**) and 3-hydroxy-1,5-benzenedicarboxylic acid

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