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C—3—5 High Temperature and High Pressure pH Sensors with Sputtered Iridium Oxide Films

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Recently the needs are increasing for devices for the direct measurement of electro-chemical properties of geothermal brines, of water in nuclear reactors and other high temperature solutions. However, no sensor is available in practical use for such applications. This paper is concerned about a new sensor for the measurement of pH of high temperature and high pressure solution. The proposed sensor ,ion controlled diode(ICD,figure 1),is principally a gate controlled diode with a pH sensitive film as a gate metal. The ICD is composed of three separate parts: gate controlled diode,chemically sensitive membrane (CMS),diffusion layer separating the insulator and the CMS. This paper mainly describes the experimental results of the pH response of electrodes consisting of d.c. reactively sputtered iridium oxide on a variety of substrates. Preliminary results about the temperature dependences of GCD and barrier layer are also presented.

Iridium oxide films were deposited by d.c. reactive sputtering from an iridium metal target in a pure oxygen plasma. The sputter deposition was done in 6x 10^{-3}torr oxygen at a power density of 0.8Wcm^{-2} for two hours. At all times the substrate temperature was maintained at less than 40°C. The resulting films were metallic dark blue and approximately 1500A thick. Film adherence was estimated by resilience to physical contact and resistance from peeling in aqueous solutions. In DI water, the adherence test was performed up to 200°C and 4000psi. Sputtered films on tantalum,stainless steel,nickel silicide,iridium and silicon adheres well ,while films on aluminum and gold did not. Mixed results were obtained with chromium,molybdenum and silicon dioxide substrate. The typical results of the measurement of open circuit cell potential versus pH are shown in Fig.2 ,the potential, E,of as-prepared electrodes has the theoretical Nernst form,namely

$E = E_0 - (2.303\ kT/q)\ pH$........(1) with E_0 800mV related to SCE. After stabilization due to aging the slope of the pH response remained unchanged but E_0 shifted to a new value of 580 mV. This behavior is representative of all electrodes tested. This aging process,characterized by the change in E_0 with time is shown in Fig.3. Storing of electrodes at ambient temperature in room air or DI water leads to a gradual (a few hours to a few days) change of E_0. Exposure to DI water at elevated temperature and pressure also resulted in accelerated aging as shown by the behavior of electrode #Ta 6 in Fig.3. The initial pH response of this electrode was Nernstian with E_0~720mV. Immersion in 160°C ,4000psi water for two hours resulted in a negative E_0 shift,but no loss of slope of the room temperature pH response. However, a subsequent 2 hours in 200°C,4000psi water resulted in virtually no further change. In Fig.4,typical temperature dependance of pH response slope are shown for aged electrode (Ta substrate). The results show that the response slope is slightly less than predicted by equation 1 at elevated temperature,whereas standard potential (E_0) has little temperature dependence. The various ionic interferences were found to be acceptable for a practical use. Sodium ion interference was a small positive shift in E vs.pH(less than 10mV at[Na^+] below 0.1 M for all temperature tested) with little associated change in slope. The effect of dissolved Pb^{++},Fe^{+++},Fe^{++},$Cu^+$and Ag^+ was essentially negligible at concentrations ut to 10^{-2}M. The worst case produce 8mV positive shift in potential.

A series of experiments for the temperature dependence of the gate controlled diode showed that the GCD is a useful vehicle to construct an ion sensor up to 250°C. The experimental results and the related modelung is published elsewhere.

As a barrier layer,metal silicide was found to be a promising candidate for high pressure and temperature applications. Preliminary results showed that nickel silicide is stable enough in the water at 200°C and 4000 psi. Some other metal silicides are now on research program for this application.

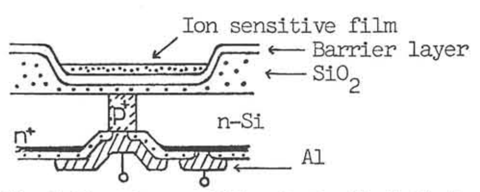

Fig.1 Structure of Ion Controlled Diode

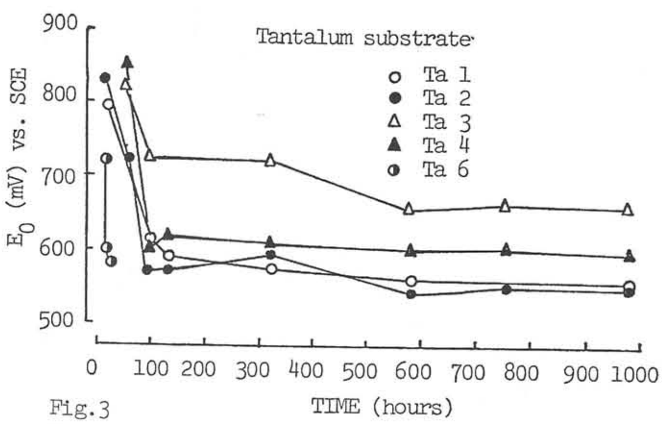

Fig.3
Variation of standard potential, E_0, with time of sputtered iridium oxide electrodes on Ta substrates.

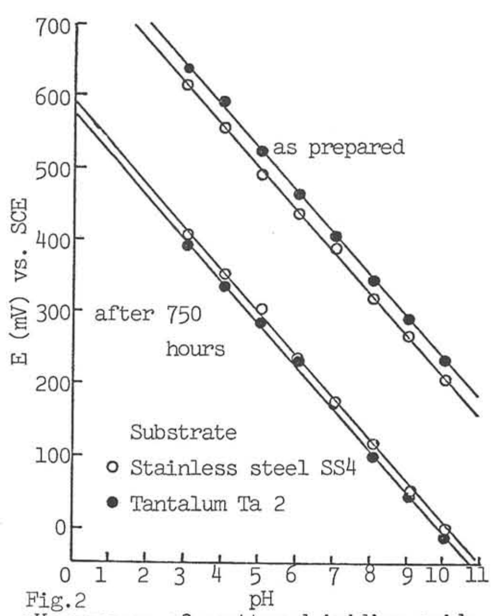

Fig.2
pH response of sputtered iridium oxide

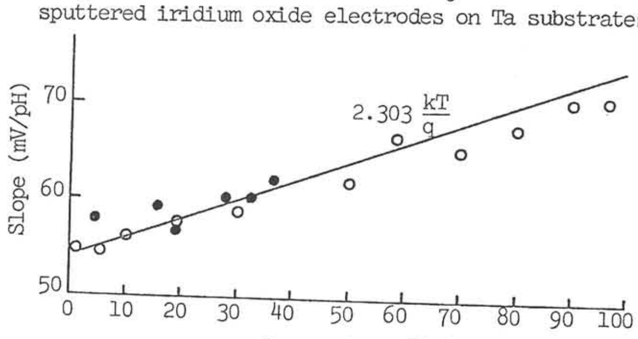

Fig.4
pH response slope as a function of temperature;
--- buffered solution, --- unbuffered solution.