Studies on Platinum Coating on Zirconia Substrate of Oxygen Sensors using Four-Point Probe and AC Impedance Technique

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Oxygen is vital to a large variety of well-known industrial and life processes that involve oxidation and combustion. The most widely used in situ analysis of oxygen at high temperatures is using a solid state electrolyte galvanic cell made of yittria-stabilized zirconia with porous platinum coated on its both sides, i.e., Pt | P_{O2}(I, process)| Y_2O_3-ZrO_2| P_{O2}(II, air)| Pt. The electron-transfer reaction, e.g., $O_2 + 4e \rightarrow 2O^{2-}$ or $2O^{2-} - 4e \rightarrow O_2$, happens on the anodic and cathodic interfaces of platinum/zirconia, respectively. The solid state electrolyte zirconia carries through oxygen ion O^{2-}. The open-circuit potential of the galvanic cell relates to oxygen concentrations by Nernst equation. It is noted that the thickness of the porous platinum coating is vitally important for the galvanic cell. If it is too thin, the galvanic sensor may give a weak and unstable signal for oxygen concentration, and the lifetime of the sensor will be very short. If it is too thick or too dense, this may block oxygen transfer across the electrode/electrolyte interface that is also detrimental to the sensor functionality. There exists an optimum thickness for the sensor performance. However, no reports have been found regarding a convenient and rapid method to monitor or determine the thickness during the coating preparation. In this work a four-point probe is used to determine the thickness of the platinum coating on zirconia disks or tubes as shown in the drawing below (Fig. 1). Solartron technique of AC impedance measurement is also employed in this study.

It is known that the resistance of a film is directly proportional to the resistivity, ρ, and inversely proportional to the thickness, d. Therefore, the resistance of a sheet (a thin film) is defined as R_s, which is equal to ρ/d. With the four point probe technique, the film resistance is measured by passing a fixed known current through two points, and measuring the voltage at two other points, as shown in the drawing below. The constant current is "injected" on the leftmost pin, and "withdrawn" at the rightmost pin, and the voltage is then measured across the two center pins. If the distance between the pins is equal to "a", the voltage measured should be,

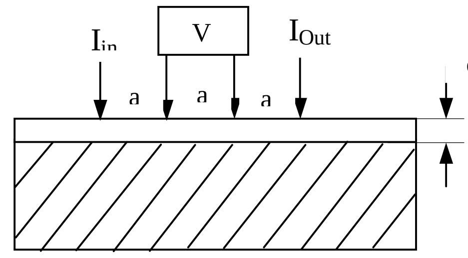

Figure 1. An outline of four-point probe

$$V = \int_a^{2a} j(x)\rho\, dx = \int_a^{2a} \frac{I}{\pi\, x d}\rho\ dx = \frac{\rho}{d} I \frac{\ln 2}{\pi}$$

$$d = \frac{\rho \ln 2}{\pi}\left(\frac{I}{V}\right) \quad or \quad R_s = \frac{\pi}{\ln 2}\left(\frac{V}{I}\right)$$

where j(x) is the current density.

The resistivity of pure platinum is 0.107 Ohm-µm at 25°C. The thickness of platinum coating can be calculated from I-V measurement by the four-point probe based on the above equation,

Each platinum-coated zirconia cell is measured with four-point probe and impedance technique. A typical result is shown in Fig. 2. One can see that a thicker coating, identified by the four-point probe, gives a narrower AC impedance spectrum, indicating a smaller electrode resistance. It was found that a cell showing a narrower spectrum has better functionality and a longer lifetime in lab accelerated life tests. It is concluded that use of four-point probe can determine the thickness of the platinum coating on zirconia substrate and predict the sensor functionality; the coating thickness can be made to an optimum level through the four-point probe measurements.

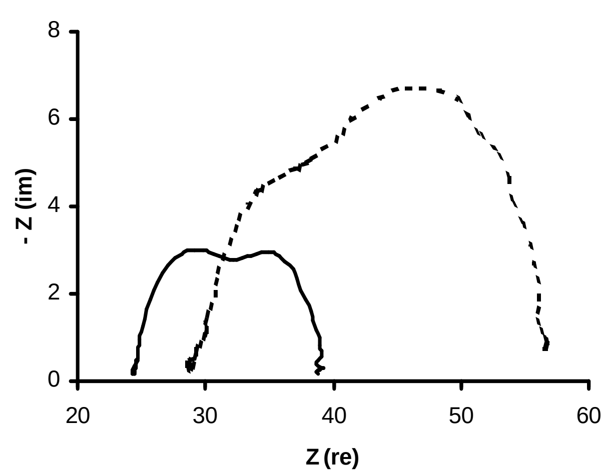

Figure 2 Impedance spectra of cells with thin Pt coating (dash line) and thick Pt coating (solid line) determined by four-point probe.