Point Electrode Studies of the Solid Electrolyte–Electrode Interface

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In the development of new electrode materials for high temperature Solid Oxide Fuel Cells methods are needed for the electrochemical evaluation of the catalytic properties of the materials. A major problem in the comparison of materials is how to determine the geometry and the effective length of the active reaction zone, the triple phase boundary. One way of solving this is by the application of point electrodes where the electrode-electrolyte contact is assumed to be circular with a radius calculated from the high frequency impedance. The perimeter is the taken as the length of the reaction zone. A condition for this to work in a reproducible manner is that the properties of the reaction zone are stable.

Recent studies have shown that the activity of the reaction zone is influenced by the electrode reaction itself and changes in the morphology have been observed by AFM (1,2,3). As consequence results may be masked by memory effects. The aim of the present work is clarify to what extent the picture of a point electrode as a surface in intimate contact surrounded by a reaction zone is influenced by these processes, and to obtain more information on the mechanisms. The basic idea is that if the change in reactivity is due to changes in the interface structure, i.e. increase of the triple boundary length by roughening of the interface, a change in the interfacial capacity pr. projected contact area would be expected.

A number of impedance measurements is carried out on small spherical (~ 1mm diameter) platinum electrodes mounted in a thin alumina tube resting on a polished 8 mol% yttria stabilized zirconia electrolyte at 1000°C in air. The results where analysed in terms of the equivalent circuit $R_{YSZ}(R_rQ)$ in the frequency range 0.5MHz–1kHz.

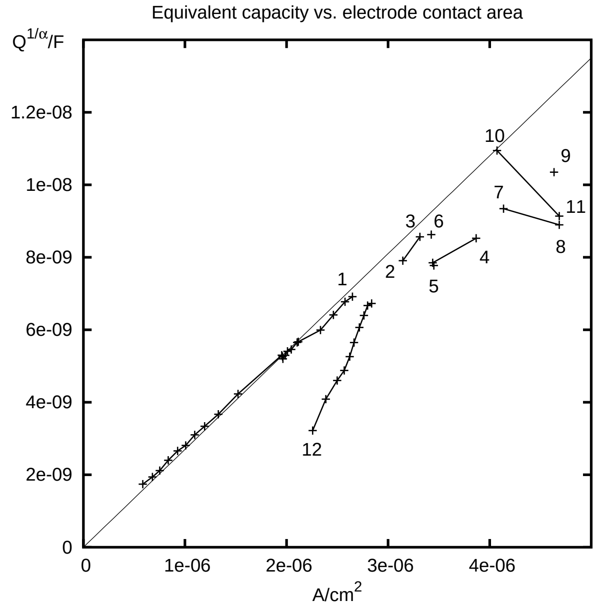
Fig. 1 shows the equivalent capacity, $C^{1/\alpha}$, plotted against the contact area during an experimental period of 2 weeks. The contact area is calculated from the electrolyte resistance as $A = 1/(4\pi(\sigma R_{YSZ})^2)$.

After the electrode has been allowed to touch the electrolyte an increasing capacity proportional to the contact area is seen. This reflects the plastic deformation of the platinum sphere due to the weight of the alumina tube (5 g).

Next, a number of experiments, to be reported in more detail, is carried out. After each of these the impedance is again determined at the equilibrium potential at 1000°C in air. The different perturbations are indicated on the graph by numbers.

1-2 Thermal cycle at equilibrium. Determination of activation energies.
3-4 Potential step to -0.150 V for 5 hours. Activation.
5-6 Potential staircase 0 → -0.150 → 0.050→ -0.150
6-7 Potential step to 0.050 V for 4 hours. Activation.
8-9 As 5-6.
9-10 Thermal cycle at -0.150 V. Activation energies.
11-12 Strong anodic activation due to computer communication error.

It is seen that as long as the electrode is kept at the equilibrium potential, the capacity pr. unit area is constant, indicating a stable reaction zone. Polarising the electrode a decrease in this ratio is observed. Although capacities calculated from CPA elements can be questioned, this indicates a change in the interfacial structure. It is noted that after the strong activation in step 11-12 the interface slowly (timescale of days) relaxes toward the equilibrium.



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