Fluctuations at Electrode – YSZ Interfaces

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From experiments on electrodes on YSZ surfaces it is well known that a short current or overvoltage pulse can decrease the interfacial impedance leading to an temporary increase in performance [1, 2]. This sensitivity to the pre-history is probably one of the explanations for the discrepancies between results reported for single electrode studies.

The mechanism behind the activation is still an unresolved problem. In the case of point electrodes, i.e. electrodes with a very small electrode – electrolyte contact area, more or less regular fluctuating patterns are observed. Probably this behavior is part of the mechanism behind the general current activation mechanism, but in the case of large porous electrodes it is only observed after a major perturbation because of the damping by the large interface.

Fig. 1 shows a slow potential sweep on a Pt point electrode on a YSZ surface. For the part of the anodic and the cathodic branches where the electrode approaches equilibrium, quadratic expressions are used as smooth approximations for the current – overvoltage relation. Subtracting the calculated curve from the experimental, the expanded plots of the fluctuations in fig. 1b and 1c are obtained. Fig. 1b shows a characteristic pattern where the numerical value of the current slowly increases for a certain time, after which it suddenly drops to a lower value. This behavior is repeated with irregular time intervals in the order of 10^3 s. In the anodic range the fluctuations appear to be more random and as seen from fig. 1c the low frequency fluctuations are an order of magnitude lower than those seen in the cathodic range. A somewhat similar behavior has been observed for LSM cathodes on YSZ.

As shown in fig. 3 spontaneous current spikes have been observed on polarized Ni anodes. In this case a sudden activation of the electrode is followed by a decay of the current. This pattern is contrary to that of the cathode where a slow activation was followed by an abrupt deactivation.

At present, it can not be ruled out entirely that the observations above are at least partially induced by external effects like discrete steps in D/A converters, duty cycles of thermo regulators, etc. But even so, the dramatic spikes seen at the Ni anode emphasizes the care that must be taken in order to obtain reproducible results from point electrode studies.

However, it is noted that Pt cathodes and Ni anodes show reverse patterns with respect to spontaneous activation/deactivation whereas the normal behavior for both electrodes is to be activated when exposed to a current pulse. This, combined with the fact that in the case of Pt electrodes the behavior is also seen at constant polarization points to the fluctuations as an inherent property of the interface.

REFERENCES

1. A.J. McEvoy, *Solid State Ionics* **135**, 331, (2000)
2. S. McIntosh, S.B. Adler, J.M. Vohs, and R.J. Gorte, *Electrochemical and Solid State Letters*, **7**, A111, (2004)

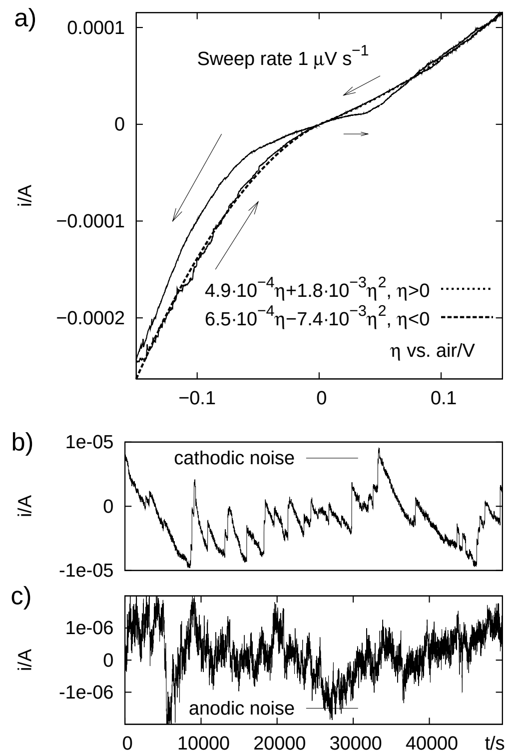

Figure 1: a) Potential sweep and smoothening relations for a Pt point electrode on YSZ in air at 1000°C. b) cathodic current fluctuations in the in the range -0.15 to -0.1 V.
c) anodic current fluctuations in the in the range 0.15 to 0.1 V.

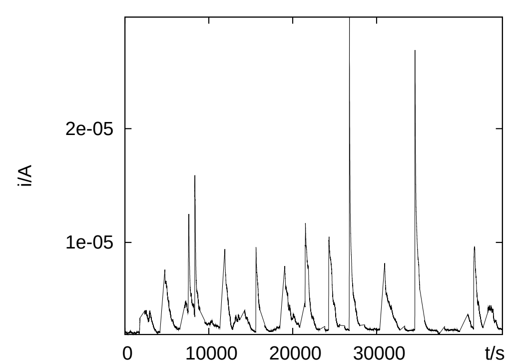

Figure 2: Current spikes on a Ni point electrode on YSZ polarised to 0.1 V in $H_2\,(97\%) + H_2O\,(3\%)$ at 1000°C.