Need for In Operando Characterization of Electrochemical Interface Features

It has proven particularly difficult to determine the electrode reaction mechanisms in high temperature solid oxide cells (SOCs) that convert gases. The literature is full of contradictory statements and apparently contradictory findings. Often the same type of electrochemical kinetics that apply to low temperature aqueous systems are assumed valid for SOCs, but in our opinion this has not been fruitful as they do not describe the experimental findings properly. Classical room temperature wet electrochemistry has experienced a huge progress in understanding of the electrode reaction mechanisms during the recent 2 decades. This progress has to a large extent been based on combination of electrochemical characterization and in situ and in operando and in situ surface analysis techniques, which so far have been less developed for high temperature electrochemistry above 300 °C. In spite that such techniques have only recently started becoming available for SOC electrochemistry, they are strongly needed. The high temperature solid-solid and solid-gas interfaces tend to change a lot over time due to segregation of electrolyte and electrode constituents and unavoidable trace impurities on a level of few ppm. Furthermore, a porous electrode for solid-gas reactions has three phase boundaries (TPBs), where the electrolyte, the electrode and the gaseous reactants meet. The current density will be concentrated around the TPB. Also, the TPB seems particularly prone to collect trace impurities and minority components, probably because the TPB zone has many sites with higher free energy relative to the rest of the electrode and electrolyte surface. An example of the segregation is the enrichment of yttria to the yttria stabilized zirconia (YSZ – the common SOFC electrolyte) surface, which takes place during a few hours at operation temperature. Furthermore, most often a silica rich layer will form on top of the yttria enriched layer. These “interphase” (not interface) layers may grow and change over time and with changes in temperature and other test conditions. Such segregation seems to be equally pronounced for surfaces and interfaces of the popular perovskite structured metal oxide electrodes such as lanthanum strontium manganites or cobaltites on which a several nanometer thick skin of strontium rich oxides forms already during cell preparation and it is believed that this is changing significantly during electrode operation. However, our knowledge about the driving forces for and the kinetics of the formation of the interphases is very superficial. Thus, there is a strong need for in operando techniques that can characterize and monitor the development of the mentioned features as function of time and changing experimental conditions with respect to electrical, structural and chemical properties at the nano-scale. Going through the various known techniques, it becomes clear that there are not sufficient in operando techniques available to make a comprehensive electrode characterization, and therefore in situ techniques are usually employed, in which at least one of the operation conditions are fulfilled, e.g. temperature but not atmosphere is matching relevant operation conditions. Finally, our analysis of already published results points out the advantage of combining several different techniques such as electrochemical impedance spectroscopy with in operando scanning probe microscopy and surface sensitive chemical analysis methods. Examples of results will be presented.

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