Estimation of Charge Transfer Resistivity of LSM/YSZ and LSC/SDC using Patterned Electrodes
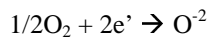
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In solid-state electrochemical devices when predominantly electronic conducting materials are used as cathode and an oxygen ion conductor as the electrolyte, it is generally assumed that the electrochemical reaction of oxygen reduction given by

$$1/2 O_2 + 2e' \rightarrow O^{-2}$$

occurs at the three phase boundary (TPB) between cathode, electrolyte and the gas phase. The corresponding geometric parameter, which governs the overall reaction kinetics, is the length of the TPB per unit area of the electrode/electrolyte macroscopic interface, given by l_{TPB} in units of cm^{-1}. The area specific charge transfer resistance may then be given by

$$R_{ct}^{TPB} = \frac{\rho_{ct}}{l_{TPB}}$$

where ρ_{ct} may be defined as the charge transfer resistivity, which may depend upon a number of parameters such as the oxygen partial pressure, electronic and ionic conductivities of the two materials, temperature, etc. However, it is microstructure-independent, and thus can be used as a figure of merit to compare two electrode materials. For a given set of conditions of temperature and atmosphere, if the electrochemical reaction occurs at a TPB, it would be expected that the polarization resistance would obey the above relationship.

When there is some transport of oxygen through the dense part of electrode, such as would occur if the electrode exhibits some oxygen ion conduction in addition to its electronic conduction (that is, mixed ionic-electronic conduction, MIEC), then the total area specific charge transfer resistance, R_{ct} is given by

$$\frac{1}{R_{ct}} = \frac{1}{R_{ct}^{TPB}} + \frac{1}{R_{ct}^{MIEC}} = \frac{l_{TPB}}{\rho_{ct}} + \frac{A_A}{R_{ct}^{MIEC}}$$

where, A_A is the area fraction of the electrode (microscopic electrode-electrolyte contact area), R_{ct}^{MIEC} is the area specific charge transfer resistance associated with the through transport of oxygen.

In real electrodes which may consist of porous composite mixtures of electrocatayst and electrolyte, the length of TPB can not be directly determined, although it can be estimated using techniques in quantitative stereology. This in fact has been done in a limited number of studies.

From an experimental standpoint, however, a direct approach would be to deposit the electrode material, e.g. LSM or LSC in a specific geometric pattern over an electrolyte disc, e.g. YSZ, or SDC and measure the polarization resistance using techniques such as impedance spectroscopy. Such an approach has been used recently. The present study was undertaken to investigate charge transfer characteristics at a LSM/YSZ/gas phase and LSC/SDC/gas phase TPB using patterned electrodes.

Electrolyte (YSZ or SDC) discs of approximate diameter 24 mm and thickness 3.5 mm were fabricated using conventional ceramic processing methods involving die-pressing of powder compacts followed by sintering in air. One surface of each disc was polished. Masks corresponding to wide range of TPB were fabricated. Using these masks, patterned working electrodes (LSM and LSC) (Figure 1) were deposited on the polished surfaces, in a circular area of 1 cm diameter at the center of the discs, using photolithographic techniques. A counter electrode of platinum was applied on the opposite face using platinum paste, again in a circular area of 1 cm diameter at the center of the discs so that it is symmetric with respect to the working electrode. A platinum reference electrode in the form of a ring was attached along the cylindrical surface of the disc. Impedance spectroscopy was used to obtain the polarization resistance to investigate the LSM-YSZ and LSC-SDC half cell reactions at temperatures between 650-800°C and p_{O_2} between 10^{-3} to 1 atm.
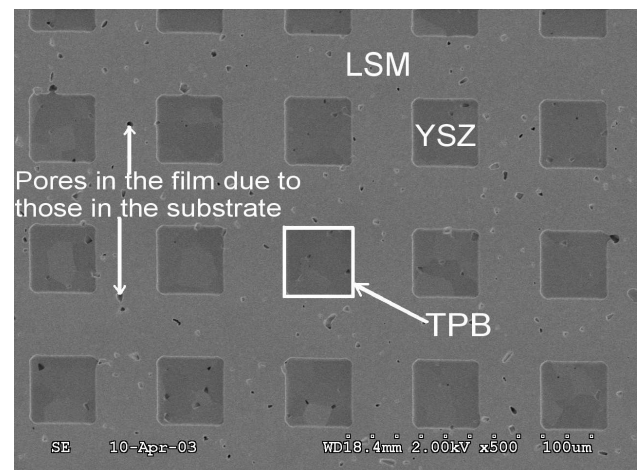

Figure 1. SEM of an LSM electrode on YSZ