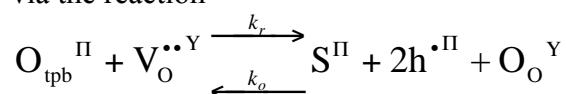


Competition Between Oxygen Reduction Pathways in SOFC Cathode Materials.
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Debate exists over the mechanism by which oxygen reduction occurs at cathodes used in solid oxide fuels. The traditional mechanism involves reduction of oxygen at the triple phase boundary. Adler and co-workers^{1,2} formalized a second mechanism which involves reaction of adsorbed oxygen with vacancies in cathode materials with mixed electronic-ionic conduction (MEIC). Sunde and co-workers^{3,4} described the steady state current-voltage response for these pathways in two separate manuscripts. They denoted the traditional TPB reaction as “Reduction of Adsorbed Oxygen” (RAO) and the newer pathway as “Direct Vacancy Exchange” (DVE). In this work, we describe how the over-potential at the cathode–electrolyte interface influences the relative competition between these two pathways.

Fig. 1 shows the two major pathways proposed for a MEIC contacting an oxygen ion conducting electrolyte. In both pathways, oxygen is first adsorbed on the pore wall at a vacant adsorption site. The adsorbed species may be partially reduced by electrons from the MEIC. In the RAO pathway adsorbed oxygen diffuses along the pore wall to the TPB where reduction occurs via the reaction



in which Y denotes the electrolyte phase and Π denotes the MEIC. In the DVE pathway a similar non-electrochemically activated reaction occurs with vacancies in the MEIC. The exchange of vacancies across the MEIC-Electrolyte is the active electrochemical step. Following Sunde and co-workers^{3,4} the mass transfer properties of the system can be described by two coupled non-linear differential equations. The major difference lies in the description of the MEIC-electrolyte interface and the influence on the boundary conditions.

The potential drop across this interface must be identical for the two electrochemically activated reactions. The over-potentials are related by

$$\eta_{\text{RAO}}^{\text{BV}} = -\frac{RT}{2F} \ln \frac{C_v^{\Pi} (1 - \theta^{\text{oc}\Pi}) \theta^{\Pi}}{C_v^{\text{oc}\Pi} (1 - \theta^{\Pi}) \theta^{\text{oc}\Pi}} + \eta_{\text{DVE}}^{\text{BV}}$$

where θ is the fraction of occupied oxygen adsorption sites and C_v is the vacancy concentration.

This relationship is used in the RAO and DVE Butler-Volmer equations to obtain the relative currents for the two pathways. The logarithmic term represents the concentration over-potential from the equilibrium condition and changes as mass transfer effects modulate the vacancy and adsorbate concentrations at the surface. In effect as one pathway dominates, the associated concentration over-potential will increase and force more current flow through the alternate pathway.

1. S.B. Adler, J.A. Lane, B.C.H. Steele, J. Electrochem. Soc., 143 (1996) 3554.
2. S.B. Adler, Solid State Ionics, 111 (1998) 123.
3. A.M. Svensson, S. Sunde, K. Nisancioglu, J. Electrochem. Soc., 144 (1997) 2719.
4. A.M. Svensson, S. Sunde, K. Nisancioglu, J. Electrochem. Soc., 145 (1998) 1390.

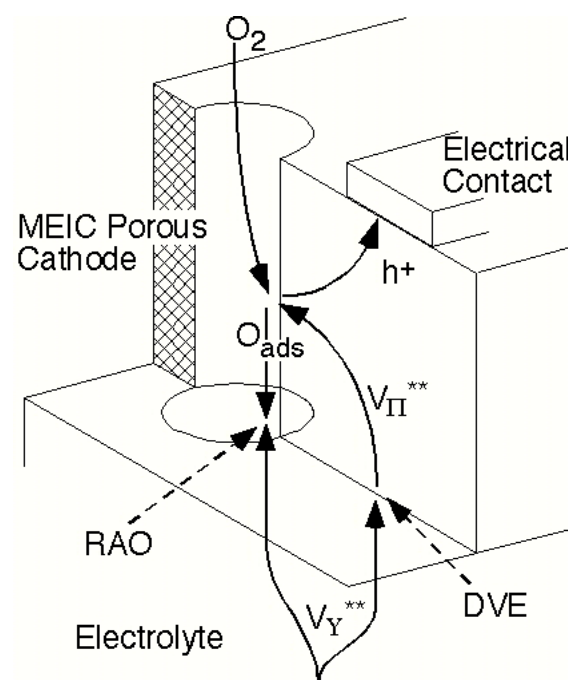


Figure 1. Schematic of the reduction of adsorbed oxygen (RAO) and direct vacancy exchange (DVE) pathways on a mixed electronic-ionic conductor.