# Mechanism of oxygen electrode delamination in solid oxide electrolyzer cells

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## ABSTRACT

An electrochemical model for degradation of solid oxide electrolyzer cells is presented. The model is based on concepts in local thermodynamic equilibrium in systems otherwise in global thermodynamic non-equilibrium. It is shown that *electronic conduction* through the electrolyte, however small, must be taken into account for determining local oxygen chemical potential, $\mu_{O_2}$, within the electrolyte. The $\mu_{O_2}$ within the electrolyte may lie out of bounds in relation to values at the electrodes in the electrolyzer mode. Under certain conditions, high pressures can develop in the electrolyte just near the oxygen electrode/electrolyte interface, leading to oxygen electrode delamination. These predictions are in accord with the reported literature on the subject. Development of high pressures may be avoided by introducing some electronic conduction in the electrolyte.

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## 1. Introduction

### 1.1. Solid oxide electrolyzer cell (SOEC) degradation

Considerable work has been reported on the use of solid oxide electrolyzer cells (SOEC) for electrolysis of $H_2O$ for hydrogen generation [1–17]. Typical SOEC consists of an oxygen ion conducting solid electrolyte such as yttria-stabilized zirconia (YSZ) sandwiched between two electrodes; steam-$H_2$ electrode (which is the cathode in SOEC) made typically of nickel + YSZ and oxygen electrode (which is the anode in SOEC) made typically of an electron (hole) conducting perovskite such as Sr-doped $LaMnO_3$ (LSM) mixed with YSZ. The cell is typically operated over a temperature range from 800 to 900 °C. Water vapor containing sufficient amount of hydrogen to prevent oxidation of Ni is circulated past the steam-$H_2$ electrode. Externally applied DC voltage greater than the decomposition potential of $H_2O$ is applied across the cell such that $H_2O$ is decomposed at the steam-$H_2$ electrode forming hydrogen with oxygen transported (as ions) through the electrolyte towards the oxygen electrode and electrons

transporting in the external circuit. The viability of SOEC for hydrogen generation as a practical system, however, has not been demonstrated in long term testing since SOEC cells do degrade over time, and it is known that the degradation rate is typically greater than solid oxide fuel cells (SOFC), which often are identical (or similar) cells but operated in the power generation mode. In SOEC, one of the modes of failure has been reported to be the occurrence of delamination of the oxygen electrode [6–10]. As an example of the morphology of oxygen electrode delamination in SOEC, Fig. 1 shows an SEM micrograph (Fig. 9 of Reference [10]) of a delaminated oxygen electrode from reference [10]. The principal objective of this manuscript is to propose a fundamental mechanism of degradation of solid oxide electrolyzer cells (SOFC), which explains the observed delamination of the oxygen electrode.

### 1.2. Global non-equilibrium, local equilibrium

The mechanism is based on the very fundamentals of non-equilibrium thermodynamics and transport theory. The approach used in this manuscript is similar to the one used
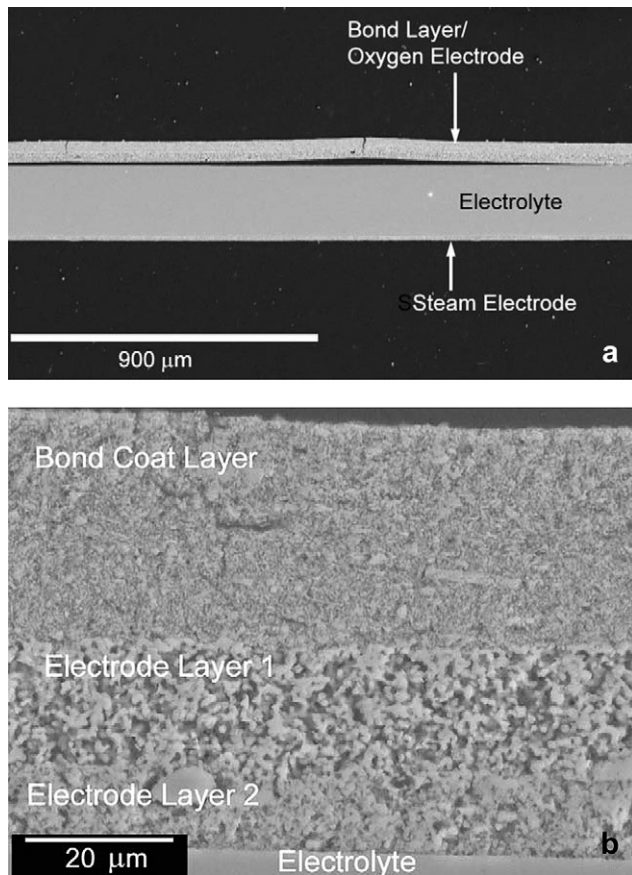
**Fig. 1 – SEM micrographs from Mawdsley et al. [10] showing oxygen electrode delamination along the oxygen electrode/electrolyte interface.**

previously by the author for studies on transport through predominantly ionic conductors and degradation of solid oxide fuel cell stacks [18,19]. The approach is based on the incorporation of the local equilibrium criterion into the transport equations [18,20]. Much of the work on transport is based on linear, non-equilibrium thermodynamics. All reported work on transport through solid electrolytes and mixed ionic electronic conductors is based on either explicit or implicit assumption of local equilibrium, even though the implications of this very important assumption are rarely addressed. Recent non-equilibrium molecular dynamics (NEMD) simulations in several systems have shown that local equilibrium is applicable to a very vast majority of the systems that are in global thermodynamic non-equilibrium [21–23]. An important consequence of the existence of local equilibrium in solid electrolytes is that electronic conduction cannot be assumed to be identically zero even in a predominantly ionic conductor [18]. This is a subtle but a very important point. Yet in many studies, contradictory assumptions of the simultaneous existence of local equilibrium (often tacitly made or even apparently unknowingly made) and purely ionic conduction (no electronic transport) are made [24].

In studies in the general area of non-equilibrium thermodynamics, the concept of local equilibrium has been the cornerstone of many advances and has been extensively discussed in the literature. The general conclusion of this enormous body of work on non-equilibrium thermodynamics is that local equilibrium is almost always valid, even in cases involving nonlinear, non-equilibrium thermodynamics. In fact, there are very few (possible) cases in which local equilibrium may be violated. These are very rare and not encountered in cases involving transport of matter by diffusion. Thus, insofar as transport is concerned, there appear to be no reported cases in which local equilibrium is violated. A possible violation of local equilibrium is synonymous with inability to uniquely assign a temperature to a point in the system [20]. As to how rapidly local equilibrium is typically achieved can be understood by an example of a quantity of a gas. Suppose molecules are assigned some arbitrary initial velocities that do not fit the Maxwell distribution. Molecular dynamics calculations show that within a few collisions the distribution becomes Maxwellian − and results in a locally well-defined temperature [20]. Similar reasoning is applicable to solids with atoms treated as linear harmonic oscillators. All known transport studies assume that there is a well-defined temperature at a point in the system at a given time, whether it is fixed in time (steady state) or varies with time (transient state). Thus, all transport studies assume local equilibrium.

The basic concept of local equilibrium, extensively discussed in textbooks on irreversible thermodynamics, is that even in systems not in global equilibrium Gibbsian laws of thermodynamics are applicable to microscopic volumes suitably chosen [20]. This is the criterion of local equilibrium in an otherwise global non-equilibrium. In such cases, all extensive thermodynamic functions are replaced by their local densities [20]. This formulation dates back to the 1930s with the classic papers by Onsager. In what follows, we will examine the implications of local equilibrium in predominantly oxygen ion conductors in a globally non-equilibrium state, which forms the basis for the proposed electrode delamination model.

### 1.3. Non-equilibrium thermodynamics, local equilibrium and transport in predominantly oxygen ion conductors

We consider an oxygen ion conductor with cation sub-lattice virtually immobile. In an oxygen ion conductor, the existence of local equilibrium with respect to oxygen is described by [25,26]
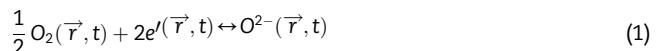
$$\frac{1}{2} O_2(\vec{r}, t) + 2e'(\vec{r}, t) \leftrightarrow O^{2-}(\vec{r}, t) \tag{1}$$

which leads to

$$\frac{1}{2}\mu_{O_2}(\vec{r}, t) + 2\mu_e(\vec{r}, t) = \mu_{O^{2-}}(\vec{r}, t) \tag{2}$$

or

$$\frac{1}{2}\mu_{O_2}(\vec{r}, t) + 2\tilde{\mu}_e(\vec{r}, t) = \tilde{\mu}_{O^{2-}}(\vec{r}, t) \tag{3}$$

where $\mu_i(\vec{r}, t)$'s are the local (function of position) chemical potentials at time $t$, and $\tilde{\mu}_i(\vec{r}, t)$'s are the local electrochemical potentials given by $\tilde{\mu}_i(\vec{r}, t) = \mu_i(\vec{r}, t) + z_i F \Phi(\vec{r})$ for species $i$ where $z_i$ is the valence (including sign), $F$ is the Faraday constant and $\Phi(\vec{r})$ is the local electrostatic potential. There is no time dependence in $\Phi(\vec{r})$ since we are only considering