A plethora of phenomena associated with oxygen vacancies in oxides

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1. Introduction

Despite existence of other types of defects, oxygen vacancies are often regarded as the prototypical defects in oxides. They may form due to intrinsic disorder, but most frequently they are the consequence of doping (or impurities) and/or oxygen non-stoichiometry due to neutral oxygen release or incorporation. The latter comes along with additional electronic defects and leads to mixed ionic and electronic conductors (MIECs). Oxygen vacancies without additional electronic defects are essential in electrolytes for solid oxide fuel or electrolysis cells (SOFCs/SOECs), e.g. YSZ (yttria stabilized zirconia). Highly doped MIECs with oxygen vacancies, on the other hand, are common electrode materials for SOFCs/SOECs. Also in insulating materials for dielectrics or piezoelectrics oxygen vacancies may exist due to doping or non-stoichiometry. Here, they are mostly unwanted and may cause degradation, for example in SrTiO$_3$ (STO) and Pb(Zr,Ti)O$_3$ (PZT). Even cation conducting materials such as Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) may exhibit a substantial amount of oxygen vacancies, see below. This tremendous importance of oxygen vacancies in solid state ionics has lead to many scientific studies and numerous details of oxygen vacancy formation, oxygen vacancy transport and oxygen vacancy reaction are well understood.

However, novel or uncommon aspects of oxygen vacancies in oxides can still be discovered and this presentation gives a series of examples on such phenomena for a broad range of oxide materials, from MIECs to pure oxide ion conductors, insulators or cation conductors. This also shows that we are still far from a complete understanding of the colorful world of oxygen vacancies in oxides, particularly in oxides upon voltage or light and in oxides with extended defects such as grain boundaries or dislocations. A few examples of interesting phenomena due to oxygen vacancies in LSF, LSC, LSM and STO are briefly discussed in the following, further examples on PZT, LLZO and YSZ are only mentioned but will be detailed in the talk.

2. Results on oxygen reduction and evolution reactions in SOFCs/SOECs

Oxygen reduction or evolution at MIEC electrode surfaces, e.g. on Sr-doped LaFeO$_{3-δ}$ (LSF) or LaCoO$_{3-δ}$ (LSC), are at the very heart of many SOFCs and SOECs and the corresponding reaction rates are decisive for the efficiency of these electrochemical cells. Hence, a mechanistic understanding of such electrode reactions is crucial.
However, despite the seemingly simple situation involving only one diatomic gas molecule, a clear mechanistic picture of this surface reaction is still missing. This is partly due to the fact that established concepts of electrochemical kinetics, such as Butler-Volmer’s equation describing rate limiting charge transfer in aqueous solutions, cannot be applied [1,2]. Moreover, it is highly challenging to identify the mechanistically meaningful reaction order of oxygen gas species, since oxygen not only affects adsorbates but also the concentrations of the reacting defects such as oxygen vacancies or electron holes. As an example, Figure 1 displays the reaction rate for oxygen reduction at a LSF thin film electrode on YSZ electrolyte for different oxygen partial pressures. Surprisingly, the oxygen reduction current for a given overpotential hardly increases for increasing oxygen partial pressure. The effective reaction order of oxygen is thus close to zero, i.e. apparently oxygen does not affect the rate of oxygen reduction.

![Graph showing current density vs. overpotential for different oxygen partial pressures](image)

Figure 1: Dependence of the oxygen reduction current on oxygen partial pressure and overpotential for a LSF thin film electrode on YSZ electrolyte, measured at 600°C. The sketch indicates in red the relevant part of the reaction at the LSF surface and the effects of $p(O_2)$ and $\eta$.

This unexpected result, however, can be understood when re-analyzing the data in a different manner. Instead of plotting the current for fixed overpotential $\eta$, we may also plot the current for fixed oxygen chemical potential in the LSF electrode. It means that we use the overpotential to counter-balance any change in partial pressure according to Nernst’s equation and thus defect concentrations remain constant while the oxygen partial pressure is varied. Such a re-analysis reveals that the almost negligible partial pressure dependence is due to a counter-balancing of two opposite partial pressure effects: Higher oxygen pressure helps oxygen reduction by supplying more oxygen molecules, but higher oxygen partial pressure also hinders oxygen reduction by annihilating the essential oxygen vacancies for oxide ion incorporation, cf. Figure 1.

Another only partly understood aspect of oxygen reduction is the role of the exact chemical surface composition and structure and reasons behind degradation. Sr segregation is known to play a detrimental role [3] but in some studies severe degradation is also found without detected surface composition changes.
For a more detailed analysis of the role of cations on oxygen reduction kinetics, we combined the possibility of cation surface modification by pulsed laser deposition (PLD) with in-situ impedance spectroscopic analysis of the resulting electrochemical surface kinetics (Figure 2). These measurements confirmed the detrimental role of Sr and the accelerating effect of Co for LSC thin film electrodes. However, surprisingly already very tiny amounts of Sr lead to severe degradation; for example a single PLD pulse on a SrO target, leading to 4% of a monolayer of SrO on LSC, increased the polarization resistance by more than 40%. This strongly suggests that some very active sites exist on LSC surfaces and those are deactivated by Sr deposits [4].

![Diagram of impedance analysis setup](image)

Figure 2: L.h.s.: Sketch of the set-up for in-situ impedance analysis during PLD for measuring effects of cations on oxygen reduction kinetics of LSC thin films. R.h.s.: Tracer diffusion profiles of epitaxial LSM on LaAlO₃ (LAO) with apparent uphill diffusion after annealing.

In a third example it is shown that not only grain boundaries in Sr doped LaMnO₃ (LSM) [5] but also dislocations in epitaxial LSM films display fast oxygen diffusion paths. Depending on the dislocation distribution, these fast diffusion paths may even lead to apparent up-hill diffusion in oxygen tracer profiles, see Figure 2 r.h.s. [6].

3. Results on oxygen vacancies in SrTiO₃ upon light and voltage
When combining a SrTiO₃ single crystal with a thin YSZ film (Figure 3), a voltage results upon UV light at ca. 400°C. Interestingly, after switching off the light a battery-type voltage remains in the few 100 mV range. This voltage is caused by oxygen incorporation upon UV, leading to vacancy concentration changes in SrTiO₃. After illumination, the oxygen chemical potential in SrTiO₃ is thus enhanced compared to the outer atmosphere [7]. Accordingly, a kind of light-driven charging of an oxygen battery can be realized in this way. The stoichiometry change upon illumination is also reflected by a drastic conductivity enhancement of the SrTiO₃ electrode, which only very slowly relaxes after illumination. Also, a continuous operation of this cell is possible with oxygen pumping under UV.

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Oxygen vacancy concentrations in STO can also be affected by applying a voltage. STO thin films with one ion blocking electrode (Nb-doped STO substrate) therefore build-up an oxygen stoichiometry gradient upon a field. Interestingly, the time dependence of this vacancy gradient formation is reflected by an inductive loop in an impedance spectrum (see Figure 3) and the ionic conductivity of the film can be determined from the loop [8,9]. Other oxygen vacancy related effects refer to tracer diffusion in doped Pb(Zr,Ti)O₃ (PZT), where donor doping leads to accumulation space charge layers and acceptor doping causes less oxygen vacancies than expected [10]. In LLZO, on the other hand, oxygen vacancies are often neglected but recent measurements using tracer diffusion indicate very significant oxygen vacancy concentrations that may also affect the Li ion conductivity [11]. For YSZ, finally, the well-known change of the activation energy in Arrhenius plots for oxygen ion conduction is reconsidered and a novel interpretation is suggested [12].

Figure 3: L.h.s. Battery type voltage, resulting for a thick STO electrode on a YSZ electrolyte (see inset) after illumination. R.h.s. Impedance spectrum of a Fe-doped STO thin film on Nb-doped STO substrate, measured with a LSC microelectrode at ca. 600°C upon 300 mV bias.

References