surface thermodynamics at SOFC/SOEC electrodes under electrochemical reaction conditions [1,2]. Spectroelectrochemical methods, i.e. electrochemical control and characterization simultaneously with spectroscopic monitoring with X-ray absorption spectroscopy (XAS) X-ray photoelectron spectroscopy (XPS) or Raman spectroscopy (RS) at high temperatures (HT). These techniques are very promising for characterization of surface properties like oxidation states, surface polarization, surface coverage with adsorbate, etc. at real or almost real working conditions. Single chamber (SC) two-electrode in situ near ambient pressure (NAP) XPS has been applied to monitor different aspects of some SOFC electrode materials and has been demonstrated to be powerful method [3]. Electrode and cell electrode designs are demonstrated so far, nevertheless, there is no XPS as well as XRD measurements of SOFC and SOEC electrodes performed using controlled electrochemical potential versus well-known reference electrode, for example vs. Pt/Pyro at \( pO_2 = 0.2 \). This study presents novel three electrode dual-chamber in operando HT-NAP-XPS spectroelectrochemical SOFC measurement cell and in operando HT-XRD measurement cell and deals with electronic changes of O, Ce and Ni at electrode outer surface occurring simultaneously with changes of impedance characteristics during NiO-GDC reduction to Ni-GDC. Structural characterization of Ni-GDC cermet electrodes using dual-chamber in operando HT-XRD was also performed under different electrical loads of Ni-GDC as SOFC anode.

References

I-9.29/O
Synthesis and characterization of the novel KNiFe$_2$O$_4$-type oxide Pt$_2$Ni$_3$Co$_2$O$_{12}$

Christian Berger, Anna Theresa Strasser, Nina Schrödl, Andreas Eiger, Johannes Hörger, Edith Bacher, Werner Sitt
Montanuniversität Leoben, Chair of Physical Chemistry, Franz Josef-Straße 11, Leoben, Austria
E-mail: christian.berger@unileoben.ac.at

Rare earth nickelates \( A_{x}B_{y}O_{3+n} \) \( (A=Ln, \text{ Pt, Ni}, B=\text{ Ni} \geq n=1, 2, 3 ...) \) are among the most promising materials when high oxygen diffusivities, good electronic and significant ionic conductivities are required. Possible applications include electrode materials for intermediate temperature solid oxide fuel and electrolyzer cells, ceramic membranes for selective oxygen separation, electrochemical oxygen sensors, and heterogeneous catalysts. However, the oxygen exchange kinetics of these materials is frequently limited by the surface exchange process, which represents a drawback for many applications. In this context, catalyst substitution offers an opportunity for tailoring the material properties. For instance, it was previously reported that the incorporation of cobalt on the B-site of \( \text{La}_{2}\text{NiO}_{4+\delta} \) leads to an increase in the surface exchange coefficient of oxygen [1].

In the present study Pt$_2$Ni$_3$Co$_2$O$_{12}$ (PNO), which shows fast oxygen diffusion and high electronic and ionic conductivities, is substituted with Co to obtain Pt$_2$Ni$_3$Co$_2$O$_{12}$ (PNO), a material which should combine fast surface exchange kinetics with the favorable properties of undoped praseodymium nickelate. PNO powders were synthesized via a freeze drying process by mixing and rapid freezing of the aqueous metal acetate solutions, vacuum freeze drying of the resulting precursor, and thermal treatment to obtain the KNiFe$_2$O$_4$-type oxide. A major advantage of this method, compared to sol-gel processes such as the glycine-nitrate route, is the opportunity to produce substantial amounts of chemically homogeneous single phase powder in one batch. The calcined powder was ball milled until a monomodal submicron particle size distribution was obtained. X-ray powder diffraction and Rietveld refinement confirmed that the material was single phase with an orthorhombic KNiFe$_2$O$_4$ unit cell. Precision thermogravimetry at 30 °C to 900°C showed an irreversible mass increase at \( T \geq 750°C \) and \( pO_2 = 0.2 \) bar which indicates the transition to a higher order Ruddlesden-Popper phase \( \text{Pt}_2\text{Ni}_3\text{Co}_2\text{O}_{12} \) and PtO, in analogy to the previously described phase decomposition of PNO [2]. Differential scanning calorimetry in pure Az showed a thermal effect at \( T = 440°C \) which may be ascribed to a structural phase transition from the orthorhombic to the tetragonal modification, which was also reported for PNO [3].

References

I-9.30/O
In-situ Studying and Modifying Surface Chemistry of Perovskite-Type Electrodes under Electrochemical Operation

Alexander E. Osip
Vienna University of Technology, Institute of Chemical Technologies and Analytics, Getreidegasse 9/164-EC, 1010 Vienna, Austria
E-mail: alexander.osip@tuwien.ac.at

In case of most common fuel cell oxide fuel cell cathodes surface chemistry plays a crucial role for their electrochemical performance. On \( \text{La}_0.8\text{Sr}_0.2\text{CoO}_3 \) (LSC) for example, segregation of SO to the surface was shown to tremendously affect the surface exchange resistance\[2\]. The exact degradation mechanism associated with SO accumulation, however, is still not completely understood. One reason for this lack of knowledge is that analyzing or modifying the LSC surface was often conducted ex-situ. Thus, the investigated surface was not necessarily in the same chemical state than it had been under operation conditions.

In this contribution, the modification of the surface composition of LSC cathodes was performed by pulsed laser deposition while in-situ monitoring their electrochemical performance at elevated temperatures by impedance spectroscopy. With this method it could be proven that already very small amounts of SO cause severe deactivation of the surface, thus identifying the causes of the kinetic loss of LSC coming from only a few highly active surface sites. Moreover, cobalt oxide deposition causes reactivation, suggesting that the active sites are strongly related to Co being present at the surface.

Another promising application of perovskite electrodes is as cathode in solid oxide electrolysis cells. Besides being less prone to oxidation-induced performance degradation than common Ni/YSZ, this class of materials offers another highly interesting opportunity: Under reducing conditions perovskites containing reducible transition metals can form metallic particles on the surface—often referred to as exsolutions\[8\]. These metallic particles can exhibit high catalytic activity, thus severely affecting the electrode kinetics.

Here, the electrochemically driven exsolution of metal particles from different perovskites is monitored in-situ by near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS). When performing water electrolysis a significantly higher reaction rate was observed for exsolution-decorated electrodes. Moreover, CO\(_2\) electrolysis was performed on perovskite-type oxides with the surface chemistry of the working electrode being studied again in-situ by NAP-XPS. In this case the polarization induced formation of different carbon species—a carbonate and graphitic carbon—was observed. While the carbonate is regarded as an active intermediate in the CO\(_2\) reduction mechanism the quick removal of graphite upon retraction of the voltage demonstrates the high catalytic resilience of the perovskites.

References

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Microstructural and electrochemical degradation of infiltrated SOFC anodes

Antigoni Bertzi, Kristina Karth, Enrique Ruiz-Trigo, Farid Tarig, Vladimir Vynnyk, Nigl P, Brandau
Imperial College London, Department of Earth Science and Engineering, SW7 2AZ, London, UK
E-mail: antigoni.bertzi@imperial.ac.uk

The polarization resistance of solid oxide fuel cell (SOFC) anodes can be significantly reduced by infiltrating nickel nanoparticles into an ion-conducting ceramic scaffold, thus allowing operation even at intermediate temperatures. However, the stability of infiltrated anodes is still too poor to be used in real applications as the performance undergoes a rapid degradation \[1\], whose causes are still unclear.

In this study we present an experimental/modelling approach to quantify the different contributions that lead to the rapid increase in anode polarization resistance. YSZ symmetric cells with scandia-stabilised zirconia (ScSZ) scaffolds were impregnated with different volume fractions of Ni and anodized at constant temperature while recording the impedance every 30 mins in reducing atmosphere. The 3D microstructure...