Observation of Nickel Oxidation and Reduction Using Transmission X-ray Microscopy

Andrew M. Kiss[1], William M. Harris[1], Arata Nakajo[1], Steve Wang[2], Joan Vila-Comamala[2], Alex Deriy[2], and Wilson K. S. Chiu[1*]

[1]Department of Mechanical Engineering
University of Connecticut
Storrs, CT 06269-3139 USA

[2]Advanced Photon Source
Argonne National Laboratory
Argonne, IL 60439 USA

[*]Corresponding Author: wchiu@engr.uconn.edu

SOFCs operate at elevated temperatures, typically ranging from 800 to 1,000 °C, which allows the use of lower cost catalyst materials such as nickel. The high temperatures can accelerate phenomena such as coarsening and oxidation in fuel cell materials which can greatly affect the microstructure and performance. Nickel oxidation is one of the degradation mechanisms which is studied because of its effect on electrode performance. When nickel is oxidized, there is roughly a 70% increase in volume. The change in volume increases stresses in the electrode which can lead to electronically insulating regions, cracks, and failure of the electrode (1). By understanding these degradation mechanisms, fuel cell systems can be better optimized for performance and longevity.

The electrodes in SOFCs typically have small features which can be best imaged by the use of a microscope that can reach submicron spatial resolution. Previous techniques to measure oxidation and reduction of nickel in situ, such as thermogravimetric analysis, do not allow for the reaction to be imaged while the reaction is occurring. To accomplish this, a synchrotron-based full-field transmission x-ray microscope (TXM) was used with x-ray absorption near edge spectroscopy (XANES) to measure the reactions (2, 3). The TXM is capable of reaching tens of nanometer resolution and transmission images can be acquired during the reaction to measure absorption changes (4). The chemical composition of the sample can be verified using XANES to confirm the chemical species and complete conversion (5).

To consider oxidation and reduction processes, the sample would need to be exposed to a controlled environment. One challenge in achieving this is the limited working distance that is permitted between the optics of the TXM. In a small volume, the sample needs to be heated to temperatures approaching 1,000 °C while the appropriate gas is fed to the sample. This is accomplished using a fiber heater along with a custom made sample holder. This heater is capable of providing a large heated area that has a uniform temperature in the viewing area. This provides the flexibility for the sample to move a few millimeters and maintain a constant temperature. The gas environment is controlled by feeding oxidizing, inert, and reducing gases into the heater chamber. The sample holder was designed to feed the gas over the sample to allow for the reaction. Allowing the system to reach thermal equilibrium greatly simplifies data collection since the sample is not moving and can be kept in the field of view more easily.

Using this setup, a process is described such that oxidation and reduction reactions of nickel can be recorded. XANES scans are used before and after each experiment to confirm a complete conversion between nickel and nickel oxide (NiO). Taking projection images during the reaction is able to capture changes in volume and shape of the particles as well as changes in x-ray absorption. The x-ray source is set to an energy level such that the absorption of nickel and NiO are different and absorption changes can thus be related to reaction rates.

References:

1. D. Sarantaridis, R. A. Rudkin and A. Atkinson, J.Power Sources., **180**, 2 (2008).

2. Q. Shen, W. Lee, K. Fezzaa, Y. S. Chu, F. De Carlo, P. Jemian, J. Ilavsky, M. Erdmann and G. G. Long, Nucl. Instrum. Methods Phys. Res., **582**, 1 (2007).

3. A. M. Kiss, W. M. Harris, S. Wang, J. Vila-Comamala, A. Deriy and W. K. S. Chiu, Appl.Phys.Lett., **102**, 5 (2013).

4. J. Vila-Comamala, Y. Pan, J. J. Lombardo, W. M. Harris, W. K. S. Chiu, C. David and Y. Wang, J. Synchrotron Radiat., **19**, 5 (2012).

5. G. J. Nelson, W. M. Harris, J. R. Izzo Jr., K. N. Grew, W. K. S. Chiu, Y. S. Chu, J. Yi, J. C. Andrews, Y. Liu and P. Pianetta, Appl.Phys.Lett., **98**, 17 (2011).

Acknowledgements:
Financial support from the National Science Foundation (Award CBET- 1134052) and an Energy Frontier Research Center on Science Based Nano-Structure Design and Synthesis of Heterogeneous Functional Materials for Energy Systems (HeteroFoaM Center) funded by the US Department of Energy, Office of Science, Office of Basic Energy Sciences (Award DE-SC0001061) are gratefully acknowledged. Portions of this research were carried out at the Advanced Photon Source supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract No. DE-AC02-06CH11357.