Ambient Pressure Photoemission Investigations on PEM Fuel Cells in Operando Conditions

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Introduction and Objectives

The hallmark in the field of surface chemistry and catalysis is the understanding of the role of the chemically active surfaces in operational conditions. Ultra high vacuum based XPS has been utilized extensively to characterize the composition and the electronic properties of the surfaces but its role in explaining the chemical function is to justify the stationary properties of the catalyst surfaces. It is a very well-known fact that in operational conditions; as the surfaces are at equilibrium with the gas or liquid phase interacting with, they are prone to change. Ambient Pressure Photoemission Spectroscopy (APPES) is a rather new type of an approach that makes in-situ XPS studies near ambient conditions possible.

Understanding the catalytic cycle of the oxygen reduction reaction (ORR), identification of the nature of the surface species in mass transfer limited and zero current regimes are important objectives in the improvement of fuel cell technology. Thus, investigations on the electronic and structural properties of the adsorbates and of catalyst materials on cathode and anode side of the PEMFCs in-operando conditions, i.e. as the fuel cell is running, is crucial.

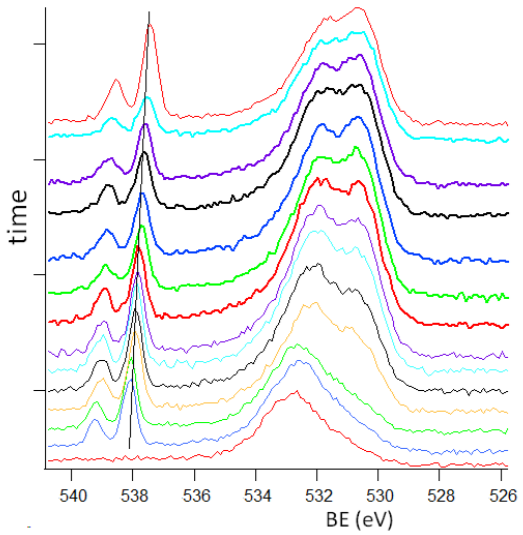
We have studied the ORR reaction on Pt PEMFC in various operational conditions using APPES technique. Depending on the operational regime, we identified surface species present of Pt nanoparticles on PEMFC cathode.

Results and Discussion

APPES system located at Stanford Synchrotron Radiation Lightsource (SSRL, Beamline 13.2) houses a gas cell inside a chamber with differential pumping units. PEMFC samples can be transferred into the gas cell that contains a small nozzle required for acquiring photoelectrons emitted from the surfaces. Currently, XPS measurements can be performed in gas ambient up to 50 torr. As well as XPS, x-ray absorption measurements can be performed in near-ambient conditions.

Our prototype cell comprised a Nafion® membrane covered on both sides with carbon-supported Pt nanoparticles. The device was humidified by supplying water vapor from the

anodic side of the membrane. The XPS spectra shown in figure below were collected while exposing the cathode to increasing pressures of oxygen gas (up to 5–10 torr) while recording the cell voltage and current. Clear changes in the composition of surface species as a function of both time and oxygen pressure are observed as the system moved from the kinetic- to the mass-transfer-limited regime. This is the first time in which the oxygen reduction reaction of a polymer electrolyte fuel cell has been measured in situ and in operando, and this is just the first of many systems that we will be able to probe by combining electrochemistry with APPES technique.



O 1s spectra as a function of time. The probed cathode surface was exposed to 0.4 Torr O_2 while the anodic surface was exposed to 40 Torr of forming gas. The sample moves from a kinetic-limited (bottom) to a mass-transfer-limited (top) regime.

The evolutions of the spectral feautures indicate that oxygen chemisorbed on Pt nanoparticles is correlated to the changes in the potential, i.e. different operational regimes of the fuel cell. Under the conditions studied formation of oxide was not observed.