

# In-situ/operando soft x-ray spectroscopy characterization of interfacial phenomena in energy materials and devices

Yi-Sheng Liu<sup>a,c</sup>, Per-Anders Glans<sup>a</sup>, Timothy S. Arthur<sup>b</sup>, Fuminori Mizuno<sup>b</sup>, Chinglin Chang<sup>c</sup>, Way-Faung Pong<sup>c</sup>, and Jinghua Guo<sup>a,d,\*</sup>

<sup>a</sup>Lawrence Berkeley National Laboratory, 1 Cyclotron Rd., Berkeley, CA 94720, United States;

<sup>b</sup>Toyota Research Institute of North America, 1555 Woodridge Ave, Ann Arbor, MI 48105, United States; <sup>c</sup>Department of Physics, Tamkang University, Tamsui 251, Taiwan; <sup>d</sup>Department of Chemistry and Biochemistry, University of California, Santa Cruz, CA 95064, United States

## ABSTRACT

Many important energy systems are based on the complexity of material architecture, chemistry and interactions among constituents within. To understand and thus ultimately control the energy applications calls for in-situ/operando characterization tools. Recently, we have developed the in-situ/operando soft X-ray spectroscopic systems for the studies of catalytic and electrochemical reactions, and reveal how to overcome the challenge that soft X-rays cannot easily peek into the high-pressure catalytic or liquid electrochemical reactions. The unique design of in-situ/operando soft X-ray spectroscopy instrumentation and fabrication principle and one example are presented.

**Keywords:** In-situ X-ray Absorption Spectroscopy, Catalysis, Photoelectrochemistry, Hematite, Water splitting

## 1. INTRODUCTION

Interfacial phenomena are crucial in verity of energy devices and chemical reactions. For example, metal ion batteries, catalysis and photoelectrochemical cells. The chemical reactions and Charge Transfer happened at the solid-liquid or solid-gas interfaces determine the functionality during operational condition. Synchrotron based soft X-ray spectroscopy has shown that its abilities for characterizing the chemical species, chemical bonding and charge transfer states in terms of electronic structure. However, X-ray spectroscopy needs to be performed under Ultra High Vacuum (UHV) environment. It makes the X-ray spectroscopy measurement under working condition of the real devices. By designing a series of in-situ cells that are able to adopt many different fields of in-situ experimental research, we are able to expose the key interfaces for measurements, such as the static/flow liquid electrochemical cells for batteries, photosynthesis applications, as well as high temperature catalysis reactions in flow gas cell.

Observation in the macroscopic scale of interests relies on the visible light that the wavelength is comparable to the size of objects. However, for micro/nano-scale and electronic structure, X-rays offer the unique investigation with element selectivity and chemical sensitivity. X-ray is covering a wide wavelength from soft (10 nm) to hard X-ray (a few pm), which can be chosen to employ in varying purposes. For example, the commercial in-house X-ray machine provides fixed specific wavelength such as Al, Cu K<sub>α</sub> incident X-ray for characteristic of crystal structure in x-ray diffraction. However, the increasing demands for higher resolution and intense X-ray sources are needed to meet the requirements of leading-edge experiments. Synchrotron has been found that it is a very promising tool for creating intensive light to meet the experimental requirements. The 3<sup>rd</sup> generation synchrotron radiation facilities nowadays provide intense light source to probe the interactions between photons and matters such as electronic structure. Especially, the tunable monochromatic and near coherent light are very powerful to understand individual elements in a tiny focused area on the samples. In addition, the nature of the uncharged photon is also a benefit for spectacular experimental needs such as applying external electric, magnetic field and simulated solar light/laser illumination on matters without any inferences. Combine these advantages above; the synchrotron radiation is suitable and perfect for the state-of-art researches such as battery, catalyst, biological researches [1-4]. Also thanks to the rapid improvement of experimental instruments, the well-developed high efficiency detectors and specialized sample holders to make the outstanding in-situ researches possible. The in-situ sample holders have been designed for varying experimental needs such as liquid, gas phase samples that will be shown in the next section. Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory, Berkeley, California is one of the brightest light sources in the world. In the ALS, we are dedicated to in-

situ/in-operando soft x-ray spectroscopies at beamline 8.0.1 and beamline 6.3.1.2. Beamline 8.0.1 is an Undulator insertion device beamline that provides 1000 times higher in intensity compare to bend magnet beamline 6.3.1.2. The photon energy range at this beamline 8.0.1 is approximately from 80 to 1400 eV that covers from all 3d transition metals L-edges up to Na K-edge. Beamline 6.3.1.2 can reach 2000 eV that is higher than that of beamline 8.0.1, which is suitable to measure XAS at the Mg, Al K-edge in Na, Mg, Al batteries research. Both beamline are equipped with photon detectors and in-situ experimental capabilities.

## 2. EXPERIMENTAL

### Soft X-ray techniques: XAS and XES

Soft X-ray spectroscopies are including X-ray Absorption Spectroscopy (XAS) and X-ray Emission Spectroscopy (XES) that allow for different experimental purposes in investigation of electronic structure of matter [5-9]. XAS and XES have been proved that their abilities and sensitivities of the chemical bonds, oxidation states, and local symmetries [10-12]. XAS is originated from a core electron absorbs a photon and transits into dipole selection rule allowed unoccupied states. Hence, XAS provides the information of the conduction band/LUMO orbital. Fig. 1(a) shows the O 1s core electron in TiO<sub>2</sub> is excited into O 2p derived unoccupied state by absorbing photons, consequently leaves a core-hole in the core level. The unstable excited core-hole state will be filled by valence band electrons during de-excitation and emit a photon that process are so-called XES, and it reflects the valence band electronic structure/HOMO information. By resonantly excited at the absorption maximum, much more detail information will be enhanced even sometimes are unable to be observed or dipole-selection rule forbidden transitions in XAS and XES such as *d-d* excitation and Charge transfer (CT) states [13]. Fig. 1(b) shows the corresponding experimental soft X-ray spectroscopy O K-edge spectra in TiO<sub>2</sub> system.

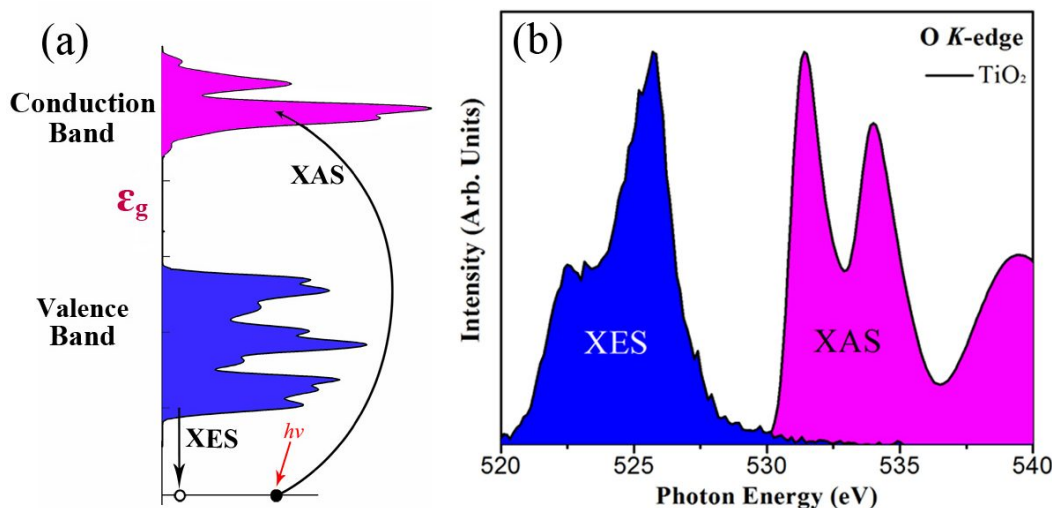


Figure 1(a) the diagram of XAS and XES process. (b) Experimental data of O K-edge XAS and XES spectra of Anatase TiO<sub>2</sub>.

### In-situ cells

Recently, the rapid growth of renewable energy and catalytic researches are urgent to be understood, that makes in-situ soft X-ray spectroscopies getting prominent. Under real reaction conditions and time frame, to monitor and clarify the evolution of electronic structure at the interfaces are the key to learn the reaction mechanisms. In next section, we are going to introduce in-situ cells that we used at the ALS for in-situ soft X-ray spectroscopy.

Understanding the dynamics at taking place molecular level in materials suitable for the applications of energy-conversion and energy-transport (e.g. *photovoltaics*, *photocatalysis* and *battery*) in real-time is of great interest in order to further improve their efficiencies and longevity. Moreover, it is even more important to be able to study the same when the specimen is in nearly identical to operational mode under ambient conditions. This has however long been

impeded given the ultra-high vacuum conditions typically required by soft X-ray spectroscopy. The introduction of the liquid cell has opened many new and exciting avenues for in-situ/operando studies of e.g. electrochemical cell that was not possible before. The effort has been evolved as a result of intense multidisciplinary collaboration at Lawrence Berkeley National Laboratory over the last decade.

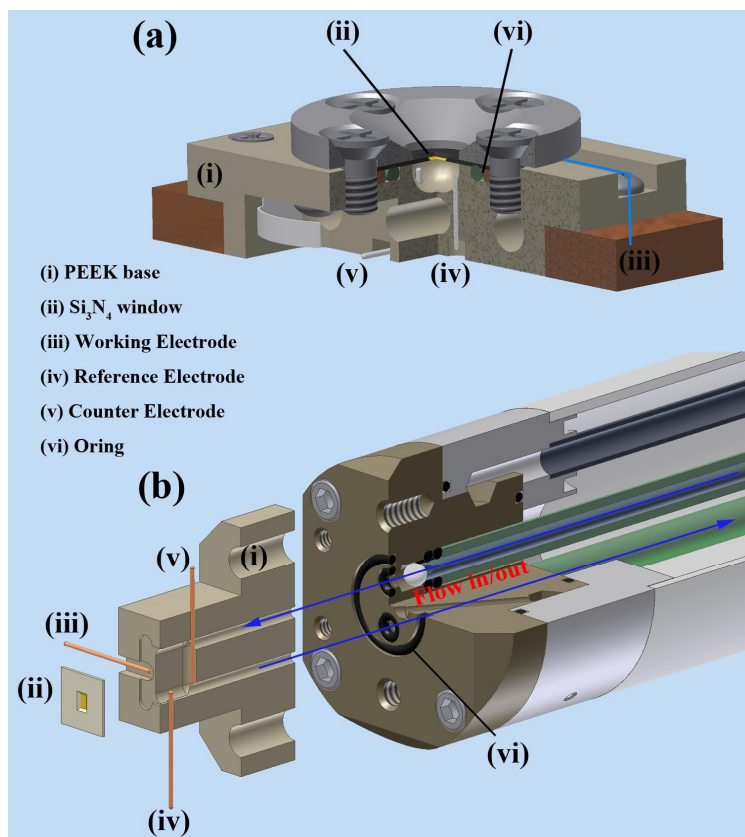


Figure 2 (a) Electrochemical static liquid cell and (b) electrochemical flow liquid cell. Note: (i) PEEK base, (ii)  $\text{Si}_3\text{N}_4$  membrane, (iii) working electrode, (iv) counter electrode, (v) reference electrode and (vi) O-ring, respectively.

These cells are composed of a polyether-ether ketone (PEEK) body separated from the otherwise UHV vacuum chamber by a 100 nm  $\text{Si}_3\text{N}_4$  membrane/window (typically  $1 \times 1$  mm) to attain UHV compatibility, and enable spectroscopic studies of liquid and gas samples under UHV conditions.

While the first generation liquid cell were known as “statics cells” [14-16] i.e. liquid samples could only be studied without any modification in their immediate surroundings, following further development of the same enabled the “flow cell” which allowed for probing samples under continuous gas/liquid flow.

Fig. 2 presents the principle design and the key features of these in-situ cells developed at Lawrence Berkeley National Laboratory. The electrochemical static liquid cell, Fig. 2(a) uses a thin membrane window to attain compatibility with UHV conditions of the fluorescence spectrometer and synchrotron radiation beamline. The synchrotron radiation enters the liquid cell through a 100 nm thick silicon nitride ( $\text{Si}_3\text{N}_4$ ) window and the emitted X-rays exit through the same window. The membrane window opening is used to be 1 mm x 1 mm in order to hold the liquid in a vacuum condition that is required to perform soft X-ray experiments. Furthermore, electrochemical static liquid cell embedded with three electrodes is developed for in-situ soft X-ray spectroscopy experiments. This design allows us to perform in-situ/operando electrochemistry X-ray spectroscopy measurements. There also developments on the liquid flow cells. For our design in Fig. 2(b), the central part of the flow liquid cell is similar to the earlier static cell shown in Fig. 2(a), while

liquid flow allows a sample refresh in order to eliminate the X-ray induced sample damage problem [17]. It also allows changing the liquid conditions in regards to the solvent concentration, pH, and temperature during soft X-ray spectroscopic measurements. It was designed to allow the liquid samples being refreshed in the rate of 50-200 *nl/s*. And electrode contacts were added to the liquid cells, so that the in-situ/operando soft X-ray spectroscopy experimental study of electrochemistry became possible [2, 4, 18]. Moreover, a four-units high temperature gas cell is also been developed for in-situ catalyst X-ray spectroscopy which is not shown in here. These cells are also used on BL6.3.1.2 and BL8.0.1 at the ALS [19]. In-situ soft X-ray spectroscopy study of liquids has attracted a lot of attentions, and there have been a number of efforts in dealing with molecular liquids in UHV condition [20-22]. Nowadays, since the in-situ X-ray spectroscopies are providing valuable information in chemical reactions in energy materials. The research based on in-situ X-ray spectroscopy is intensively promoted in the synchrotron radiation facilities all over the world. Hence, many of the active groups increase their effort to develop the reaction cells to accomplish the UHV compatible in-situ environments.

### 3. IN-SITU X-RAY ABSORPTION SPECTROSCOPY: MAGNESIUM BATTERY

One example will be shown in this section to demonstrate the ability of in-situ X-ray absorption spectroscopy that we have been done by using our in-situ cell. We have done a series of Mg batteries works by employing our in-situ cells under electrochemical controlled in-situ XAS at the ALS.

Arthur *et al.* used Mg electrolyte to show the capability of the electrochemical deposition by in-situ XAS [2, 23] Fig. 3(a) shows the Cyclic Voltammetry (CV) curves from their Mg battery setup that contains electrolyte:  $[\text{Mg}_2(\mu\text{-Cl})_3\cdot 6(\text{OC}_4\text{H}_8)]^+$  in the static electrochemical cell. The CVs curve reveals that the Mg deposition and dissolution from the electrolyte through the two- and three-electrode cyclic voltammetry between Pt coated working electrode and Mg foil counter and reference electrodes. Hence, the voltage of electrochemical reduction/oxidation reactions can be determined.

The Mg *K*-edge XAS spectra were collected at fixed voltages from open-circuit potential (OCP) to -400mV in order to monitor the onset of Mg deposition reactions. In Fig. 3(b), OCP XAS spectrum shows the Mg absorption spectrum mainly contributes from the electrolyte itself. With the increasing voltages, the spectra shows a strong pre-edge feature around 1304 eV that is contributed from Mg metal deposited on working electrode surface by comparing to the pre-electrochemical deposited Mg on working electrode surface. The XAS spectra energy shift is usually referring to the different oxidation states of metal ions in metal *K*-edge regime. In this case, the  $\text{Mg}^{2+}$  ions in electrolyte were reduced on the working electrode surface by controlling the voltage applied to the working Electrode. By monitoring the electrode/electrolyte interface and simultaneously controlling the Mg deposition potentials, we observed an intermediate Mg state existing at potentials before the deposition potential for Mg metal formation.

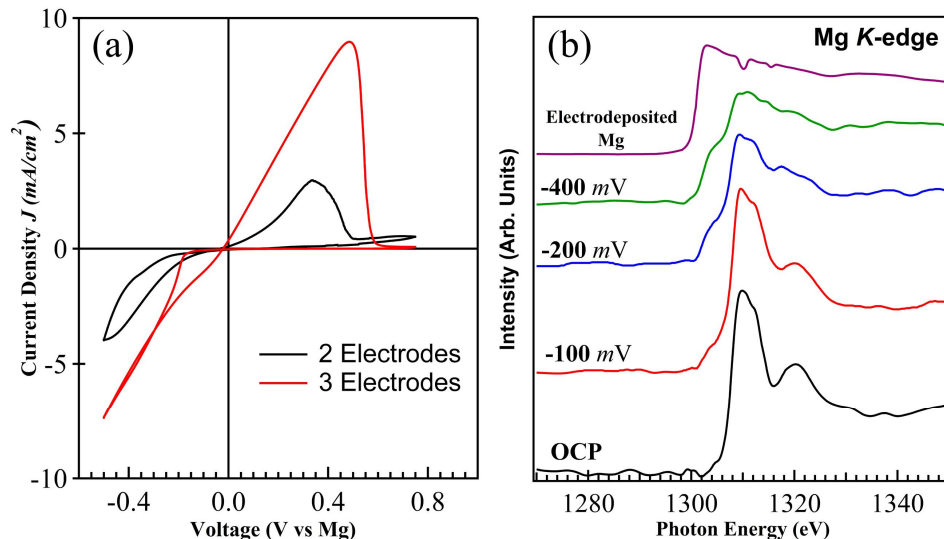


Figure 3(a) Cyclic Voltammetry with 2 or 3-electrodes setup in our in-situ cell. (b) in-situ Mg K-edge XAS spectra at different voltage points in CV curve.

From this example, we demonstrated the ability of in-situ XAS to probe Mg battery under working conditions. There are more examples such as Co/CoPt nanocatalyst reduction/oxidation under high temperature [13, 24-26], Co nanoparticles suspend in liquid solution [15], liquid water/Au interfacial structure characterization [18]. Most important example is Hematite ( $\text{Fe}_2\text{O}_3$ ) for water splitting in oxygen reduction reaction [4]. Even though the real Hydrogen evolution reaction for producing  $\text{H}_2$  are not been studied yet by using in-situ cells and in-situ XAS at the ALS. However, the goal might be achieved soon in the future since the in-situ cells or in-situ XAS are quite mature. Seeking for the suitable photoanode and photocathode material that can be adopted in our in-situ cells. Will provide fruitful information and special insights under water splitting condition by using in-situ soft X-ray spectroscopy.

## ACKNOWLEDGEMENT

The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

## REFERENCE

- [1] P. Jiang, J.-L. Chen, F. Borondics *et al.*, "In situ soft X-ray absorption spectroscopy investigation of electrochemical corrosion of copper in aqueous  $\text{NaHCO}_3$  solution," *Electrochemistry Communications*, 12(6), 820-822 (2010).
- [2] T. S. Arthur, P.-A. Glans, M. Matsui *et al.*, "Mg deposition observed by in situ electrochemical Mg K-edge X-ray absorption spectroscopy," *Electrochemistry Communications*, 24, 43-46 (2012).
- [3] J.-H. Guo, "The development of in situ photon-in/photon-out soft X-ray spectroscopy on beamline 7.0.1 at the ALS," *Journal of Electron Spectroscopy and Related Phenomena*, 188, 71-78 (2013).
- [4] A. Braun, K. Sivula, D. K. Bora *et al.*, "Direct Observation of Two Electron Holes in a Hematite Photoanode during Photoelectrochemical Water Splitting," *The Journal of Physical Chemistry C*, 116(32), 16870-16875 (2012).
- [5] L. J. P. Ament, M. van Veenendaal, T. P. Devereaux *et al.*, "Resonant inelastic x-ray scattering studies of elementary excitations," *Reviews of Modern Physics*, 83(2), 705-767 (2011).

- [6] J.-H. Guo, N. Wassdahl, P. Skytt *et al.*, “End station for polarization and excitation energy selective soft x-ray fluorescence spectroscopy,” *Review of Scientific Instruments*, 66(2), 1561-1563 (1995).
- [7] J.-H. Guo, “Synchrotron radiation, soft-X-ray spectroscopy and nanomaterials,” *International Journal of Nanotechnology*, 1(1/2), 193 (2004).
- [8] J.-H. Guo, [X-Rays in Nanoscience], Wiley-VCH Verlag GmbH & Co. KGaA, (2010).
- [9] A. Kotani, and S. Shin, “Resonant inelastic x-ray scattering spectra for electrons in solids,” *Reviews of Modern Physics*, 73(1), 203-246 (2001).
- [10] J.-H. Guo, Y. Luo, A. Augustsson *et al.*, “X-Ray Emission Spectroscopy of Hydrogen Bonding and Electronic Structure of Liquid Water,” *Physical Review Letters*, 89(13), 137402 (2002).
- [11] X. Liu, J. Liu, R. Qiao *et al.*, “Phase Transformation and Lithiation Effect on Electronic Structure of  $\text{Li}_x\text{FePO}_4$ : An In-Depth Study by Soft X-ray and Simulations,” *Journal of the American Chemical Society*, 134(33), 13708-13715 (2012).
- [12] T. S. Arthur, R. Zhang, C. Ling *et al.*, “Understanding the Electrochemical Mechanism of  $\text{K}-\alpha\text{MnO}_2$  for Magnesium Battery Cathodes,” *ACS Applied Materials & Interfaces*, 6(10), 7004-7008 (2014).
- [13] A. Augustsson, A. Henningson, S. M. Butorin *et al.*, “Lithium ion insertion in nanoporous anatase  $\text{TiO}_2$  studied with RIXS,” *The Journal of Chemical Physics*, 119(7), 3983-3987 (2003).
- [14] J.-H. Guo, Y. Luo, A. Augustsson *et al.*, “Molecular Structure of Alcohol-Water Mixtures,” *Physical Review Letters*, 91(15), 157401 (2003).
- [15] H. Liu, J.-H. Guo, Y. Yin *et al.*, “Electronic Structure of Cobalt Nanocrystals Suspended in Liquid,” *Nano Letters*, 7(7), 1919-1922 (2007).
- [16] J.-H. Guo, S. Kastanov, J. Soderstrom *et al.*, “Electronic structure study of the bases in DNA duplexes by in situ photon-in/photon-out soft X-ray spectroscopy,” *Journal of Electron Spectroscopy and Related Phenomena*, 181(2-3), 197-201 (2010).
- [17] J.-H. Guo, T. Tong, L. Svec *et al.*, “Soft-x-ray spectroscopy experiment of liquids,” *Journal of Vacuum Science Technology A*, 25(4), 1231-1233 (2007).
- [18] J.-J. Velasco-Velez, C. H. Wu, T. A. Pascal *et al.*, “The structure of interfacial water on gold electrodes studied by x-ray absorption spectroscopy,” *Science*, 346(6211), 831-834 (2014).
- [19] Y.-S. Liu, P.-A. Glans, C.-H. Chuang *et al.*, “Perspectives of in situ/operando resonant inelastic X-ray scattering in catalytic energy materials science,” *Journal of Electron Spectroscopy and Related Phenomena*, (2015). doi:10.1016/j.elspec.2015.07.004
- [20] S. Myneni, Y. Luo, L. Å. Näslund *et al.*, “Spectroscopic probing of local hydrogen-bonding structures in liquid water,” *Journal of Physics: Condensed Matter*, 14(8), L213 (2002).
- [21] C. Heske, U. Groh, O. Fuchs *et al.*, “Monitoring chemical reactions at a liquid–solid interface: Water on  $\text{CuIn}(\text{S},\text{Se})_2$  thin film solar cell absorbers,” *The Journal of Chemical Physics*, 119(20), 10467-10470 (2003).
- [22] J. B. MacNaughton, M. V. Yablonskikh, A. H. Hunt *et al.*, “Solid versus solution: Examining the electronic structure of metallic DNA with soft x-ray spectroscopy,” *Physical Review B*, 74(12), 125101 (2006).
- [23] A. Benmayza, M. Ramanathan, T. S. Arthur *et al.*, “Effect of Electrolytic Properties of a Magnesium Organohaloaluminate Electrolyte on Magnesium Deposition,” *The Journal of Physical Chemistry C*, 117(51), 26881-26888 (2013).
- [24] A. Tuxen, S. Carenco, M. Chintapalli *et al.*, “Size-Dependent Dissociation of Carbon Monoxide on Cobalt Nanoparticles,” *Journal of the American Chemical Society*, 135(6), 2273-2278 (2013).
- [25] S. Carenco, A. Tuxen, M. Chintapalli *et al.*, “Dealloying of Cobalt from  $\text{CuCo}$  Nanoparticles under Syngas Exposure,” *The Journal of Physical Chemistry C*, 117(12), 6259-6266 (2013).
- [26] S. Alayoglu, S. Beaumont, F. Zheng *et al.*, “ $\text{CO}_2$  Hydrogenation Studies on  $\text{Co}$  and  $\text{CoPt}$  Bimetallic Nanoparticles Under Reaction Conditions Using TEM, XPS and NEXAFS,” *Topics in Catalysis*, 54(13-15), 778-785 (2011).