



Electrochemical surface science twenty years later: Expeditions into the electrocatalysis of reactions at the core of artificial photosynthesis



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ARTICLE INFO

Available online 22 July 2014

Keywords:

Electrochemical surface science
Artificial photosynthesis
Water-splitting reaction
Carbon dioxide reduction reaction
Electrochemistry-surface science apparatus

ABSTRACT

Surface science research fixated on phenomena and processes that transpire at the electrode-electrolyte interface has been pursued in the past. A considerable proportion of the earlier work was on materials and reactions pertinent to the operation of small-molecule fuel cells. The experimental approach integrated a handful of surface-sensitive physical-analytical methods with traditional electrochemical techniques, all harbored in a single environment-controlled electrochemistry-surface science apparatus (EC-SSA); the catalyst samples were typically precious noble metals constituted of well-defined single-crystal surfaces. More recently, attention has been diverted from fuel-to-energy generation to its converse, (solar) energy-to-fuel transformation; e.g., instead of water synthesis (from hydrogen and oxygen) in fuel cells, water decomposition (to hydrogen and oxygen) in artificial photosynthesis. The rigorous surface-science protocols remain unchanged but the experimental capabilities have been expanded by the addition of several characterization techniques, either as EC-SSA components or as stand-alone instruments. The present manuscript describes results selected from on-going studies of earth-abundant electrocatalysts for the reactions that underpin artificial photosynthesis: nickel-molybdenum alloys for the hydrogen evolution reaction, calcium birnessite as a heterogeneous analogue for the oxygen-evolving complex in natural photosynthesis, and single-crystalline copper in relation to the carbon dioxide reduction reaction.

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1. Introduction

Electrochemical surface science, the study, at the atomic level, of the nature of the electrode-solution interface, may have enjoyed its heyday twenty-odd years ago. Much earlier, empirical research at gas–solid interfaces that sought to acquire information more fundamental than phenomenological benefitted tremendously by the establishment of stringent experimental procedures such as the use of structurally and compositionally well-defined surfaces, the vigilant control of the sample ambiance, the implementation of surface-sensitive physical methods, and the analysis of surface-reaction product distribution [1–3]. Emboldened by the remarkable advances in “dry surface science”,

a few experimentalists in electrochemistry later adopted the “surface-science protocol” in their own investigations [4–7], despite the fact that the integration of electrochemistry and surface science is far from an uncomplicated proposition. Conceptually, one has to contend with additional interfacial parameters such as solvent, electrolyte and applied potential; logistically, surface physics paraphernalia can be tremendously expensive. But the research pioneers were not only innovative, they were also persistent. Their initial successes served to motivate other investigators to take on the steep challenges by themselves and thereby expand the “moist surface science” research landscape [8–10]. Individual laboratories carried out studies in surface electrochemistry with only sparse collaborations among them.

A major portion of the earlier published electrocatalysis-surface science research, loosely marked here as investigations that observe the surface-science protocol, was focused on small-molecule reactions, such as hydrogen oxidation and oxygen reduction, directly relevant to

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the operation of fuel cells; the catalysts investigated were almost exclusively based upon precious noble metals. *Ex situ* experimental methods [4–11] included, but were not limited to, low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), high-resolution electron energy loss spectroscopy (HREELS), X-ray photoelectron spectroscopy (XPS), temperature-programmed desorption (TPD) and low-energy ion scattering spectroscopy (LEISS); *in situ* or *operando* techniques were electrochemical scanning tunneling microscopy (ECSTM) [12,13], electrochemistry (EC) and differential electrochemical mass spectrometry (DEMS) [14].

More recently, interest has shifted to reactions that may be regarded as the reverse of those in fuel cells; *i.e.*, reactions that comprise the core of artificial photosynthesis [15]: the hydrogen evolution reaction (HER), the oxygen evolution reaction (OER), and the carbon dioxide reduction reaction (CO₂RR). The need for exceptional earth-abundant catalysts is as critical as the demand for light-absorber semiconductors that can provide sufficient electromotive force for the photoelectrochemical reactions. The direction of our own work in this area has not been towards an *ab initio* search of efficient non-precious-metal catalysts, but the correlation of the activities of putative electrocatalysts with their surface physical and chemical properties, one avenue for the understanding-based discovery of novel, or the amelioration of known but less than optimal, catalysts. Systematic surface studies are carried out only for materials that have been benchmarked [16] for superior catalytic activity. To help overcome the heightened complexity of the artificial photosynthesis systems, experimental methods, some classical, others state-of-the-art, in addition to those enumerated above are utilized: surface-enhanced Raman spectroscopy (SERS) [17], polarization-modulation Fourier transform infrared reflection absorption spectroscopy (PM-FT-IRRAS) [18], scanning (SEM) [19] and transmission (TEM) electron microscopy [20], X-ray diffraction [21], and synchrotron-based X-ray techniques such as X-ray absorption spectroscopy (XAS) [22], ambient-pressure (AP) XPS [23], and resonant inelastic X-ray scattering (RIXS) [24]. The accessibility to a repository of powerful instruments, especially the expensive and expansive systems, is a major advantage of integrated research centers, or innovation hubs, that combine basic and applied research to accelerate scientific discoveries.

In the present manuscript, surface studies of three non-rare-metal electrocatalysts that impact the core reactions of artificial photosynthesis are described: Ni-Mo alloys for the HER, calcium birnessite as a heterogeneous analogue for the oxygen-evolving catalyst in natural photosynthesis, and single-crystalline Cu in relation to the CO₂RR.

2. Experimental

Ample discussions on stand-alone equipment employed in a multitude of physical-analytical investigations of catalyst surfaces have been presented elsewhere [1–3,18–24] and, hence, will not be reshaped here; only integrated systems that combine, in a single instrument, electrochemical techniques and surface spectroscopic methods will be described briefly. Custom-designed electrochemistry-surface science apparatus (EC-SSA) are shown in Figs. 1 and 2. The former is a photograph of an older EC-SSA at Texas A&M University that is compartmentalized vertically into, from top to bottom: EC ante-chamber, LEED-AES-TPD chamber, HREELS chamber, and UHV pumping system. Fig. 2 shows a schematic illustration of a recently deployed EC-SSA at the Joint Center for Artificial Photosynthesis at the California Institute of Technology that is comprised of a cluster of UHV chambers (Kurt J. Lesker, Clairton, PA), each designed for a particular function. Central to the architecture is an oblate spheroidal distribution chamber equipped with a 360°-rotatable transfer arm (UHV-Design, Laughton, East Sussex, UK) furnished with a Cardan gear mechanism that provides up to 760 mm of translation but is collapsible to provide a sweep radius of 300 mm; it makes the secured transfer of the sample to any of the chambers possible. In addition, a unique manipulator and sample-holder design offers flexibility in sample size and type, and allows multiple samples to be “parked” inside the

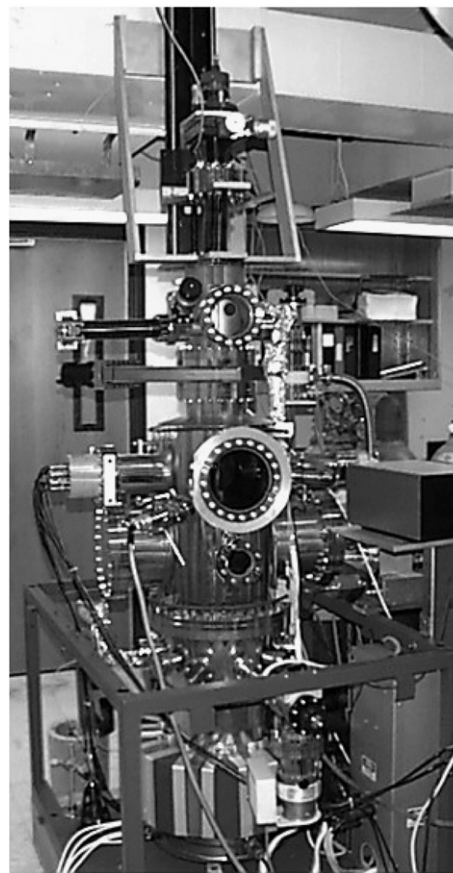


Fig. 1. Older custom-designed electrochemistry-surface science apparatus (EC-SSA). The system is divided vertically into four segments; from top to bottom: electrochemistry chamber, LEED-AES-TPD chamber, HREELS compartment and UHV pumping system.

UHV system while on queue for a specific experiment. Electrochemistry is performed by insertion of the sample into a gate-valve isolatable chamber over an EC cell in a hanging-meniscus configuration; DEMS is also done in this compartment. Catalyst preparation or surface modification is carried out in another isolable chamber equipped for physical vapor deposition and reactive sputtering. Surface characterization is undertaken in the analysis chamber that positions up to seven surface-sensitive spectroscopic modules across three levels: LEED, AES, HREELS, XPS, UPS, LEISS and TPD. The operation of an EC-SSA, as well as other discrete instruments, for electrochemical surface science investigations has been reviewed meticulously [9,25,26]; such reviews should be consulted for further details on the methodology.

In the studies described here, XRD patterns were collected using a D8 Discover diffractometer (Bruker, Billerica, MA) equipped with a Cu K α source ($\lambda = 1.5418 \text{ \AA}$) and a 2-dimensional Vantec detector. Scanning electron micrographs were obtained using a Nova NanoSEM 450 microscope (FEI, Hillsboro, OR) with an accelerating voltage of 15 kV and working distance of 5.0 mm. Low-magnification micrographs ($>10 \text{ nm}$ per pixel) were acquired with an Everhart-Thornley detector whereas higher-magnification micrographs were obtained with a through-the-lens detector. Energy-dispersive X-ray spectra (EDS) were collected in the SEM at an accelerating voltage of 15 kV using a silicon drift detector (Oxford Instruments, Abingdon, United Kingdom). AZtecTEM software (Oxford Instruments, Santa Barbara, CA) was used to interpret the EDS spectra.

XPS was carried out on an AXIS Ultra DLD instrument (Kratos Analytical, Manchester, UK) at a background pressure of 1×10^{-9} Torr. High-intensity excitation was provided by monochromatic Al K α X-rays, 1486.6 eV in energy and 0.2 eV resolution at full width at half maximum. Photoelectrons were collected at 0° from the surface normal and

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