ELECTROCHEMICAL SURFACE SCIENCE TWENTY YEARS LATER:
EXPEDITIONS INTO THE ELECTROCATALYSIS OF REACTIONS AT THE CORE OF
ARTIFICIAL PHOTOSYNTHESIS

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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; i.e., 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 escalated 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.

KEYWORDS

Electrochemical Surface Science

Artificial Photosynthesis

Water-splitting Reaction

Carbon Dioxide Reduction Reaction

Electrochemistry-surface science apparatus

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 fraction of the earlier published electrocatalysis-surface science research, loosely marked here as investigations that observe the surface-science protocol, has focused on small-molecule reactions, such as hydrogen oxidation and oxygen reduction, directly relevant to 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 (EC-STM) [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-IRAS) [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.

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 rehashed 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 Figures 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. Figure 2 shows a schematic illustration of a recently deployed EC-SSA at the Joint Center of 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 possible the secured transfer of the sample to any of the chambers. 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 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 a dozen 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 at a retarding (pass) energy of 80 eV for the survey scans; 20 eV for the high-resolution scans. The peak energies were calibrated against the binding energy E_B of the adventitious C 1s peak [1-3,26,27]. The LEISS measurements were also acquired on the Kratos instrument. A 1-keV He $^{+}$ -ion beam incident at 45° relative to the surface normal was used. LEED and AES experiments were as described previously [9,25,26].

Operando STM images were obtained with an Agilent 5500 electrochemical scanning tunneling microscope (Agilent Technologies, Santa Clara, CA) equipped with a three-electrode potentiostat. The custom-crafted electrochemical cell was made of polychlorotrifluoroethylene (Kel-F $^{\text{®}}$) fitted with a Pt counter and a Pt pseudo-reference electrode calibrated against an SHE reference cell. The STM tips were prepared by an electrochemical etch of a 0.25-mm diameter tungsten wire (Sigma-Aldrich, St. Louis, MO) in 0.1 M KOH at *ca.* 15 V. All the images were obtained with a high-resolution scanner in a constant-current mode without post-scan processes such as with high-pass filters. A bias voltage E_B of 0.5 V and tunneling current I_t of 1 nA were employed.

Unless specified otherwise, cyclic voltammograms were obtained with an SP-200 Bio-Logic potentiostat in a three-electrode configuration. For the benchtop experiments, the cell was a single-compartment glass vessel blanketed with Ar gas throughout the electrochemical experiments; the reference electrode was Ag/AgCl (1.0 *M* NaCl). For the EC-SSA work, a two-compartment cell separated by a fine-glass frit was employed [9,25,26]. The sample electrode was in one section, and both reference and auxiliary electrodes in the other; to minimize Cl⁻ contamination, the reference electrode held only 1 *mM* NaCl. The cell is inserted, through a gate valve, into the EC compartment that was backfilled with high purity Ar gas but isolated from the surface analysis chamber by a second gate valve.

RESULTS AND DISCUSSION

HER: Nickel-Molybdenum Alloys

The identification of electrocatalysts comprised of earth-abundant materials that enhance hydrogen evolution from water at high rates at low overpotentials is of fundamental importance in the development of solar-hydrogen production technology [28-32]. Nickel-molybdenum (Ni-Mo) composites are a class of materials that meets these criteria. Ni-Mo alloys and related systems have shown remarkable activity for the hydrogen evolution reaction, with current densities of 10 mA cm^{-2} at overpotentials (η) less than 0.1 V in acidic and alkaline solutions at room temperature [33-36] and up to 1 A cm^{-2} at similar overpotentials in alkaline solutions at 70 °C [37,38]. Recently, the HER activity of Ni-Mo nanopowders was shown to be comparable to that of carbon-supported Pt nanoparticles. [36].

Although Ni-Mo is among the most active hydrogen-evolution catalysts reported, the reason for its improved activity compared to that of pure Ni is not well understood [39]. Suggested rationales for the observed enhancement in activity include: (i) the M-H bond strength between Ni-Mo and adsorbed hydrogen has been optimized for the HER via the mixture of two elements on either side of the Trasatti volcano plot [34,37,40]; (ii) a spillover effect that starts with the initial formation of an M-H intermediate on Ni sites followed by the migration of the adsorbed hydrogen to nearby Mo sites where the catalytic reaction proceeds to completion [41]; or (iii) dissolution, upon initial catalyst operation, of top-layer Mo sites on porous deposits that leads to larger surface areas [42,43].

It is not possible to distinguish among the above three proposed mechanisms based solely on kinetic parameters such as the Tafel slope and exchange current density [39]. Additional investigations are required to determine surface structure and composition, and to correlate them to catalytic activity. XPS and AES are the two widely used electron spectroscopy methods for quantitative surface elemental analysis. However, neither is able to distinguish definitively between the outermost layer and the nearest sub-surface strata, a matter of major consequence in the study of reaction mechanisms at mixed metals

since the catalysis is most profoundly influenced by the nature of the topmost layer [1-3]; LEISS [44] is a more appropriate technique.

Figure 3 shows an assemblage of wide-scan (survey) and high-resolution (Ni 2p and Mo 3d) XPS spectra for a Ni-Mo alloy electrodeposit before and after acid-stability tests under the HER conditions. Since the experiments had to be performed with a rotating-disk electrode (RDE) [16], the Ni-Mo film had to be prepared outside the XPS instrument. The preparation, based upon a published procedure [45], was a cathodic electrodeposition by constant current (160 mA cm^{-2}) electrolysis for twenty minutes on a glassy carbon substrate in a solution of nickel sulfate (NiSO_4), sodium molybdate (Na_2MoO_4) and sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) in *ca.* 1 M NH_3 solution (Sigma-Aldrich, St. Louis, MO). The electrodeposit was rinsed with ultrapure ($18 \text{ M}\Omega\cdot\text{cm}$) water (Barnstead Nanopure, Thermo Scientific, Waltham, MA) prior to XPS work to remove *emersed* electrolyte. The HER stability was then carried out via controlled-current electrolysis at 10 mA cm^{-2} cathodic current density for three hours in H_2 -saturated 1 M H_2SO_4 in which the measured potential remained constant at -0.285 V (SCE); the post-HER electrode was likewise rinsed with O_2 -free ultrapure water before the XPS measurements.[†]

[†] A positive flow of H_2 gas was maintained over the RDE cell throughout the HER acid stability test. Upon completion of the experiment, the cell was sealed and placed inside the ante-chamber of a controlled-environment glove-box (Vacuum Atmospheres, Hawthorne, CA). After a 15-minute N_2 -gas purge, the cell was shuttled inside the main glove-box chamber that had 0.25 ppm of residual O_2 gas. The electrode was submerged in deaerated ultrapure water in a glass vessel fitted with a removable cap; at this point, the O_2 level was 0.35 ppm. The capped glass container was then taken out of the glove box, and the sample, covered with a protective film of pure water and under a flow of N_2 , was transferred into the XPS instrument; evacuation of the residual water took three hours. Figure 4 shows post-HER Ni 2p XPS spectra of two samples, one handled inside a glove box and the other freely exposed to the environment. Whereas solely Ni(0) existed in the former, only Ni(+3) was found in the latter, evidence of the air-sensitivity of the film.

It is clear in Figure 3 that substantial differences occur in the composition of the alloy surface, as determined from the observed binding energies, before and after the HER experiments. Two of the more significant are: (i) a preponderance of higher oxidation states of nickel (Ni^{3+}) and molybdenum (Mo^{6+}) in the freshly electrodeposited film prior to the HER; (ii) after HER in 1 M H_2SO_4 , only zerovalent Ni and lower oxidation states of molybdenum (Mo and Mo^{4+}) remained. The quantity of higher-valent species correlates with the intensity of the oxygen peak; hence, the pre-HER oxidized metals most likely exist as oxides: Ni_2O_3 , MoO_2 and MoO_3 . The changes in surface composition of the post-HER film are almost certainly a result of the cathodic reduction of the oxides:

The products of Reactions (1) to (3) are consistent with the XPS data in Figure 3. This signifies that the electrocatalyst in this particular instance is essentially a composite of two metals (Ni and Mo) and a metal oxide (MoO_2). The fact that the Ni-Mo- MoO_2 catalyst is generated from the non-catalytic Ni_2O_3 - MoO_2 -MoO deposit under the conditions of the very reaction that it is supposed to enhance is an example of *operando* electrocatalyst synthesis [46].

For the quantitative determination of the Ni(0)-to- Mo_{Total} and Mo(+4)-to-Mo(0) atomic ratios in the active catalyst, where Mo_{Total} is the sum of Mo(0) and Mo(+4), all XPS peaks were fitted to symmetric Voigt line shapes composed of Gaussian (70%) and Lorentzian (30%) functions by CasaXPS software (CASA Ltd, Teignmouth, United Kingdom) that employed a Shirley background [47]. For the two Mo peaks, fitting was constrained to maintain a 2:3 ratio between the areas of the $3\text{d}_{3/2}$ and $3\text{d}_{5/2}$ peaks and a 3.15 eV E_{B} separation; for the Ni $2\text{p}_{1/2}$ and $2\text{p}_{3/2}$ peaks, the respective constraints were a 2:1 ratio of the areas, and 17 eV separation in E_{B} . The atomic or molar ratio between Ni and Mo was obtained from Equation (4):

$$\frac{N_{\text{Ni}}}{N_{\text{Mo}}} = \frac{A_{\text{Ni}}/S_{\text{Ni}}}{A_{\text{Mo}}/S_{\text{Mo}}} \quad (4)$$

where N_{Ni} is the number of Ni atoms, A_{Ni} the area of the Ni photoemission peak, and S_{Ni} the Ni sensitivity factor; values for the latter were provided by the instrument manufacturer. Based on the data in Figure 3, the Ni(0):Mo_{Total} molar ratio was found to be 7:3; the Mo(+4):Mo(0) ratio was 1.5:1.

In this regard, it is of interest to recall results from a recent hydrogen-evolution study with Ni-Mo nanopowders synthesized by a substrate-less wet-chemical method [39]. The nanoparticles were loaded onto a Ti foil and the HER electrocatalysis was carried out in 1 M NaOH. The relevance of that work to the present discussion is the plot (Figure 5) which shows the relationship between the mole fraction of Mo in the nanopowder catalyst, as measured by EDS, and that in the precursor solution: Regardless of the Mo mole fraction in the precursor solution, the total mole fraction in the nanopowder catalyst never reached above 0.3. In addition, the catalytic activity leveled off at this same Mo concentration, a circumstance similar to that for the electrodeposited film. Since the Ni:Mo_{Total} ratios in the nanoparticles and in the electrodeposit are identical, it may perhaps be conjectured that the most efficient Ni-Mo catalyst is that which, *based on XPS or EDS*, consists of 70% Ni and 30% total Mo; this may, in fact, be the case regardless of the method of preparation (*operando* or *ex situ*), particle size (nanopowders or microcrystals) or solution pH.

It is important to underscore the fact that the elemental analysis provided by XPS or EDS is neither that of the deep bulk nor of the outermost selvage: Based on the so-called universal curve [1-3], the kinetic energies of the ejected photoelectrons, and the atomic sizes [48] of Ni and Mo, the results highlighted here are actually for the first three or four near-surface layers. If information only for the topmost layer were desired, other techniques such as angle-resolved XPS or LEISS would have to be employed.

In a LEISS experiment, the sample surface is irradiated with a beam of inert-gas ions (e.g., He⁺) of energy not higher than 1 keV, and the backscattered primary ions are energy-analyzed [44,49]. If the incident ion has a mass of M_i and kinetic energy of E_0 , and the ion backscattered at an angle θ , the total

scattering angle relative to the unperturbed trajectory of the incident ion, possesses an energy of E_1 , a classical inelastic two-collision model yields the following equation:

$$\frac{E_1}{E_0} = \left(\frac{1}{(1+A)^2} \right) \left(\cos \theta \pm \sqrt{A^2 - \sin^2 \theta} \right)^2 \quad (5)$$

where M_s is the mass of the surface atom, $A = M_s/M_1$; the positive term is for $A > 1$, and the negative term is for $|\sin \theta| \leq A \leq 1$.

Since the energy of the incident ion is relatively low, there is virtually no damage to the surface. In addition, because of the repulsive nature of the ion-atom interaction, a shadow cone is formed past the target surface atom and a blocking cone is generated at an adjacent surface atom; these cones prevent interactions between the incident ion and subsurface and limit the sensitivity of LEISS only to the outermost atoms. Sensitivity factors f for each element must be obtained by calibration (Figure 6). For a Ni-Mo film, the surface concentrations C_{Mo} and C_{Ni} can be extracted from the following equations [49]:

$$C_{Ni} = \frac{I_{Ni}}{I_{Ni} + (f_{Ni}/f_{Mo})(I_{Mo})} \quad (6)$$

$$C_{Mo} = \frac{I_{Mo}}{I_{Mo} + (f_{Mo}/f_{Ni})(I_{Ni})} \quad (7)$$

Where f_{Ni} (5) and f_{Mo} (1) are the scattering intensities for pure-metal surfaces, and I_{Mo} and I_{Ni} are the scattering intensities from the alloy (e.g., Figure 7).

Alloy buttons, prepared from ingots (Materials Preparation Center, Ames Laboratory, Ames, IA), were degreased with acetone, sonicated in an Aquanox® A4241 solution (Kyzen Corporation, Nashville, TN), rinsed with pure water and then metallographically polished. Inside the LEISS chamber, the samples were annealed at 300°C for six hours and later lightly sputtered to remove adventitious C and O. Spectra were collected at an ion-current density of 50 nA cm⁻², a condition pre-determined empirically to have no effect on the Ni:Mo ratio over the duration of the experiment: less than a 2% change in the Ni-to-Mo ratio

was noted after 100 minutes, and only five minutes are required to collect one complete spectrum. For a given sample, XPS spectra were acquired alongside the LEISS experiments; EDS measurements were also undertaken of the same sample but in a stand-alone SEM instrument.

Figure 8 shows a plot of the mole fraction of Mo at the alloy surface, as measured by XPS, EDS and LEISS, against the mole fraction of Mo in the bulk, as specified by the supplier of the alloys.[†] It is clear that, whereas the XPS and EDS results are identical and track the ideal (1:1) line, the LEISS data indicate a pronounced enrichment of molybdenum at the outermost layer. It must be stipulated, however, that this particular segment remains work-in-progress. The samples still need to be operated at hydrogen-evolution conditions. In addition, the truncation of the alloy ingots have to be controlled more stringently such that the composition at the exposed face is non-random; a well-defined single-crystal surface would serve consummately. Nevertheless, on a semi-quantitative basis, it is unmistakable that, relative to the bulk, the topmost layer of the subject Ni-Mo alloys possesses a greater fraction of Mo atoms.

OER: Birnessite as Heterogeneous Analogue for the Oxygen-Evolving Complex

A major challenge in the creation of a functional artificial photosynthesis system is the identification of robust catalysts that efficiently facilitate the light-assisted conversion of water and carbon dioxide into fuel. Efforts to meet this challenge have taken inspiration from nature. Green plants and cyanobacteria, for instance, contain Photosystems (PS) I and II that, respectively, are responsible for the formation of carbohydrates from CO₂ via the Calvin cycle and the oxygen-evolution reaction of water.

High-resolution X-ray crystallography of the oxygen-evolving complex (OEC) in PS II has revealed a distorted chair configuration of the tetramanganese monocalcium pentaoxido (Mn₄CaO₅) cluster [50]. The anodic degradation of the Mn-based molecular catalysts often gives rise to birnessite [51], a layered form of heterovalent manganese dioxide that functionally and structurally resembles the

[†] The number of data points is limited because, at ambient conditions, phase-pure compositions for Ni-Mo exist only when the fraction of Ni is below 15%, at 20%, 25%, and at 50% [49]; unfortunately, no 1:1 alloy sample was available.

OEC [52,53]. The remarkable similarity between the OEC and birnessite uniquely positions the latter to be viewed not only as a heterogeneous analogue of the former but also as a structural motif for novel OER electrocatalysts.

The mineralogical literature offers a variety of preparative routes for birnessite but the method of choice in this study is electrodeposition. The interplay of the preferred electrode, supporting electrolyte, and potential-scan rates provides access to different structures of the prepared films. Figure 9 shows the potential-current profile of a flame-annealed gold foil electrode cycled in an aqueous solution of 2 mM MnSO_4 and 15 mM CaSO_4 at a scan rate of 10 mV s⁻¹. The pH of the solution was adjusted to 5.3 via drops of freshly prepared limewater. The dotted line traces the voltammetric behavior of the electrode in blank (Mn-free) solution. The observed voltammogram displays features similar to those obtained from SnO_2 electrodes exposed to MnSO_4 in Na_2SO_4 solution [54]. The following features are prominent: (i) An initial potential scan in the positive direction yields an anodic peak at about 1.0 V, which is ascribed to the formation of birnessite. Patches of bare Au remain exposed, as evidenced by the small anodic peak at 1.1 V that is similarly found in the voltammogram of the blank. (ii) The return scan in the negative direction reveals a complex pattern of cathodic peaks associated with the stepwise reduction of Mn^{4+} into lower oxidation states until Mn^{2+} is regenerated and released back in solution. (iii) The second potential cycle shows the progressive oxidation of Mn^{2+} into the heterovalent Mn_3O_4 ($\text{MnO}\cdot\text{Mn}_2\text{O}_3$) at 0.30 V, followed by the formation of MnOOH at 0.38 V [54]. Mn_3O_4 has been noted as an anodic precursor for birnessite [55], whereas MnOOH has been used as a starting material in the single-crystal growth of birnessite [56] (iv) Respective film growth of Mn_3O_4 , MnOOH and birnessite continues with subsequent potential cycles. (v). The presence of birnessite on Au leads to an OER onset potential much earlier (less positive) than that of bare Au itself.

The above results demonstrate that birnessite can be electrochemically synthesized by either potentiostatic or potential-sweep deposition within a potential window of 0.8 V to 1.1 V, as defined by the first cycle in Figure 9. In this work, birnessite films were prepared potentiostatically at the peak potential ($E_p \sim 1.0$ V), a procedure that allows facile coulometric control of the birnessite loading on the

electrode. The films used in all spectroscopic analyses involved the passage of *ca.* 100 mC cm⁻² after 1 hour under quiescent conditions.

Morphological studies using scanning electron microscopy reveal the presence of only one phase. The observed sheet-like structure of birnessite deposited on Au, shown in Figure 10, is consistent with that of birnessite electrodeposited onto fluorine-doped tin oxide (FTO) or on SnO₂ [57,58]. The crystallinity of the potentiostatically prepared birnessite is confirmed by XRD (Figure 11), which shows a characteristic intense (001) peak that corresponds to a *d*-spacing of 7.1428 Å [59].

The choice of CaSO₄ as the supporting electrolyte in the preparation of birnessite is strategic: Under saturated conditions of CaSO_{4(aq)} (*ca.* 15 mM), Ca²⁺ becomes the predominant cation in solution, thereby promoting its intercalation between the invariably negatively charged sheets of edge-sharing MnO₆ units of birnessite. XPS results (Figure 12) clearly indicate the presence of Ca²⁺ in the prepared film. Soaking birnessite samples in a solution of foreign metal ion is a common experimental tactic to modify lamellar materials via intercalation, lattice vacancy incorporation and surface complexation [60]. Experiments on the influence of various intercalated cations on the resultant structure and reactivity of birnessite as an OER catalyst are in progress.

The catalytic performance and stability of the calcium-intercalated birnessite (Ca-birnessite) under OER conditions were tested by cycling the material in 0.1 M NaOH for two hours under an atmosphere of oxygen. A potential window between -0.7 V and 1.7 V was chosen to encompass regimes slightly beyond the hydrogen evolution and oxygen evolution reactions. Ca-birnessite exhibits an overpotential of *ca.* 620 mV needed to sustain a current density of 10 mA cm⁻². A comparison of the peak-shape nuances of the XPS Mn (2p_{3/2}) and (3s) spectra of Ca-birnessite, before and after the potential cycling in alkali, (Figure 13) suggests the instability of the prepared film. For instance, the low-energy shoulder (639 - 641 eV) of the dominant Mn⁴⁺ multiplet peaks in the Mn (2p_{3/2}) spectrum indicates changes in the Mn³⁺ concentration in the film; similar inferences can be deduced from the post-voltammetry sharpening of Mn 3s peaks [61,62].

The prospect of enhanced OER catalytic performance and stability of the birnessite motif may rely on the partial substitution of Mn with other transition metals to form multimetallic oxides. Such systematic modification is the subject of current research on multimetallic birnessite strategically intercalated with different cations.

CO₂RR: Cathodic Regeneration of Well-ordered Cu(100) from Disordered Cu(100)-O

The ability of copper electrodes to catalyze the reduction of carbon dioxide better than any single-metal material is well known [63]. However, it is also a fact that copper is an efficient scavenger of O₂ gas. Hence, the electrocatalytic reduction of CO₂ at copper must overcome the presence of surface oxides formed spontaneously when the metal is handled, unprotected, in air. In this part of the study, the structure and composition of a Cu(100) single-crystal electrode surface were tracked, via LEED and AES, from when it is oxide-coated to when it is subjected to conditions at which the CO₂RR transpires. Air oxidation was simulated by dosing the sample surface, at 25°C, with O₂ at a partial pressure of 10⁻⁷ Torr; total exposure was limited to 10⁴ Langmuirs (1 L = 10⁻⁶ Torr-sec). After examination by LEED and AES, the oxidized electrode was immersed in a solution of 0.1 mM KOH and 1 mM K₂SO₄ at -0.90 V for 180 seconds. The electrode was then *emersed* from the pH 10 solution at the same immersion potential for another set of LEED and AES measurements. The results, in terms of Auger spectra and their corresponding diffraction patterns, are summarized in Figure 14.

The data for the Cu(100) surface prepared under ultrahigh vacuum conditions by sequential ion bombardment (to remove top-layer impurities) and thermal annealing (to restore atomic smoothness) are shown in Figure 14(A). The Auger spectrum indicates that the interface consists only of Cu atoms since only Cu peaks, with the main (LMM) transition at 920 eV, are observed; the distinct LEED pattern signifies the existence of a well-ordered Cu(100) surface.

Figure 14(B) shows the Auger spectra for the Cu(100) single crystal after it is dosed with gaseous oxygen [64,65]. When compared to the AES plot in Figure 14(A), two major differences are obvious: (i) A new peak at 503 eV, attributable to the oxygen KLL transition, has emerged, and (ii) the intensities of

the Cu peaks have been attenuated by the oxide overlayer. AES peak-to-peak height measurements for O and Cu, along with the respective relative sensitivity factors of 0.17 and 0.01 were used to extract the O surface coverage in terms of an O/Cu atomic ratio; a value of *ca.* 0.12 was obtained [64]. The LEED pattern associated with this particular surface is also given in Figure 14(B). It is noteworthy that the adlattice is ordered; the structure is denoted as Cu(100)-($\sqrt{2} \times 2\sqrt{2}$)R45°-O.

The AES and LEED results after emersion at -0.9 V are displayed in Figure 14(C). The post-emersion Auger spectrum for the electrode reveals the presence of oxygen and potassium. Since the Pourbaix diagram for copper [66] indicates that, at this negative potential, the electrode surface should be completely in the zerovalent state, the O and K signals are almost certainly due to the (solidified) KOH remnant in the emersed layer. The absence of sulfur in the Auger spectrum implies that the presence of sulfate ions in the compact layer is negligible relative that of the hydroxide ions at such high alkalinity and negative potential; this behavior is not inconsistent with the facts that copper hydroxide is more insoluble than copper sulfate, and that the sulfate dianions would be more strongly repelled by a negatively charged electrode than a hydroxide monoanion. The LEED pattern for the emersed surface, Figure 14(C), reveals a highly diffuse Cu(100)-(1×1) pattern; the indistinctness of the diffraction spots is most likely due to the disordered residue of potassium hydroxide that was retained in the emersion layer.

Despite the Pourbaix-diagram evidence that, at -0.9 V in pH 10 electrolyte, bulk copper has to be in the metallic, oxide-free state, the issue of the nature (structure and composition) of the cathodically reduced Cu(100)-O electrode surface has not been decidedly resolved by LEED and AES due to inclusion of non-volatile species in the emersion process. Copious rinses with pure water to remove compact-layer interferences only lead to loss of negative-potential control that, in turn, results in the restoration of the surface oxides. It is in this regard that *operando* EC-STM experiments were carried out. Specifically, a Cu(100) electrode that had previously been exposed to ambient air for one week was imaged at high resolution while it was held at -0.9 V in a solution of 0.1 mM KOH and 1 mM K₂SO₄. The result, a steady-state atom-resolved EC-STM image, is displayed in Figure 15. While the terraces are not particularly wide, the atomic arrangement within a given terrace is well-ordered with the distance

between the atoms measured to be 2.65 Å, identical to that on a square Cu(100) net [48,67]. The regeneration of a clean and well-ordered Cu(100)-(1×1) surface by cathodic reduction of the surface oxide is thus established.

SUMMARY

Interest in electrochemical surface science had dwindled in the latter part of the past two decades, but the last few years has seen a resurgence in research activity; the studies recounted here help herald and sustain such upsurge. The present manuscript has showcased the deployment of a set of utilities in the electrochemical surface science arsenal towards the characterization of earth-abundant materials that catalyze the reactions which underpin artificial photosynthesis. Three systems are described: nickel-molybdenum composites for the hydrogen evolution reaction; calcium birnessite as a heterogeneous analogue of the oxygen-evolving complex in natural photosynthesis; and single-crystalline copper in relation to the carbon dioxide reduction reaction.

The renewed attention to surface electrochemical investigations has been driven primarily by the necessity for renewable energy sources, specifically solar-powered photovoltaic electrolysis and artificial photosynthesis, as one route to help mitigate global climate change. Several important aspects in those areas are still not well-understood and, in such predicaments, recourse is invariably sought from fundamental-science investigations. For example, the identification of electrocatalysts for the oxygen-evolution reaction may be capably pursued by discovery-science approaches like high-throughput combinatorial synthesis; but a search rooted to a basic understanding of structure-composition-function relationships for known catalysts offers a feasible, albeit a bit protracted, alternative approach. In artificial photosynthesis, concerns on the instability of photocathodes and photoanodes represent issues in corrosion science. Deleterious interactions between photoelectrode and electrocatalyst in integrated photoelectrochemistry devices typify phenomena at the metal-semiconductor interface. The heterogenization of molecular complexes is largely the formation of chemical bonds between a molecular anchor group and the atoms at the electrode surface. These and numerous other examples substantiate the prognosis that, if major advances in artificial photosynthesis are to be achieved, electrochemical surface science has to remain prominent in the investigative repertoire.

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Figure 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.

Figure 2. Schematic illustration of recent custom-designed EC-SSA. The techniques available in this single system are: LEED, AES, XPS, UPS, HREELS, LEISS, TPD, EC and DEMS. PVD and reactive sputtering are available for sample preparation or surface modification.

XPS of Ni-Mo Alloy Electrodeposited on Glassy Carbon

Figure 3. XPS of Ni-Mo composite electrodeposited on glassy carbon before and after HER electrocatalysis. Experimental conditions were as described in the text.

Ni 2p XPS of Ni-Mo After HER Stability Test

Figure 4. Post-HER XPS spectra of Ni-Mo deposit. Top: Sample handled in air. Bottom: Sample handled in O₂-free glove box. Experimental conditions were as described in the text.

Figure 5. Plot of molybdenum mole fraction in Ni-Mo catalyst nanopowder against the molybdenum mole fraction in the precursor solution. Experimental conditions were as described in the text.

Figure 6. LEISS calibration spectra for pure Ni and pure Mo at two different ion beams. Experimental conditions were as described in the text.

Figure 7. LEISS spectra for Ni-Mo alloys. The larger peak is for Ni. Experimental conditions were as described in the text.

Figure 8. Plot of mole fraction of Mo on the alloy surface, as measured separately by LEED, EDS and LEISS. The solid line represents ideal (1:1) correlation between the amount of Mo in the bulk and on the surface.

Figure 9. Cyclic voltammogram of Au in 2 mM MnSO_4 and 15 mM CaSO_4 at a scan rate of 10 mV/s. Experimental conditions are described in the text. Superimposed for reference is the voltammogram obtained from Mn-free blank solution. Geometric area of electrode = 1.0 cm².

Figure 10. Morphological analysis of Ca-birnessite on Au using scanning electron microscopy. The high-magnification image depicts the presence of only one phase.

Figure 11. X-ray diffraction patterns of Ca-birnessite on ITO. Experiments were conducted using Bruker D8 Discover diffractometer equipped with a Cu K α source and a 2-dimensional Vantec detector. Peaks associated with the substrate are designated with asterisks.

Figure 12. XPS narrow scan of the Ca 2p_{3/2} region for Ca-birnessite on Au. A Kratos Axis Ultra X-ray photoelectron spectrometer was used at a base pressure less than 10⁻⁹ Torr. Data were obtained with a monochromatic Al K α source (1486.7 eV) and a concentric hemispherical analyzer with a pass energy of 20 eV, with the photoelectrons captured normal to the surface. Binding energies were calibrated against the adventitious C 1s peak (taken as 284.65 eV).

Figure 13. XPS narrow scan of the Mn 2p_{3/2} and 3s regions for Ca-birnessite on Au before and after potential cycling in 0.1 M NaOH. Experimental conditions for the acquisition of the XPS data are the same as in the Figure 12.

LEED and AES of Clean, O₂-Dosed and Cathodically Regenerated Cu(100)

Figure 14. AES spectra and LEED spot pattern for Cu(100). (A): UHV-prepared Cu(100). (B). Cu(100) after it was dosed with O₂ gas. (C). After cathodic reduction at -0.9 V in 1 mM K₂SO₄ solution adjusted to pH 9 with KOH. Since the emersed electrode was not rinsed with water, The O and K signals are due to residual KOH retained in the emersed layer.

Experimental conditions were as described in the text.

Figure 15. *Operando* STM of a Cu(100) previously exposed to ambient air for twenty-four hours after 180 seconds at -0.9 V in 1 mM K_2SO_4 solution adjusted to pH 9 with KOH. Experimental conditions were as described in the text.