Strategies for Enabling Stable and Efficient

(Photo)Electrochemical Water Splitting

Thesis by

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Abstract

The electrolysis of water splits H_2O into its constituent parts, generating H_2 fuel and O_2 as a by-product. Although electrolysis has been known since late 1700s and has a consistently expanding industrial capacity, several barriers still exist to its widespread utilization as a clean method of generating hydrogen for industrial uses or as a grid-scale energy storage chemical. Among these, the materials and costs constraints surrounding the use of precious metal catalysts and expenses associated with balance-of-system costs are of primary importance. In this thesis, the first point is addressed by utilizing earth-abundant catalysts for chemical, electrochemical, and photoelectrochemical water splitting reactions. Specifically, Mn_ySb_{1-y}O_x catalysts were synthesized for use as both cerium-mediated chemical water oxidation catalysts and as electrochemical water oxidation catalysts, furthering steps towards removing Ir from industrial electrolysis devices. Addition of Sb was shown to stabilize reactive Mn centers in these configurations, offering enhanced stability over pure Mn oxide catalysts. Reduction of electrolyzer balance-of-system costs were addressed in this thesis through the integration of multiple components of a solar-powered electrolysis system into a single, integrated photoelectrochemical water splitting device. Specifically, electrodeposition conditions were shown to affect the spontaneous mesostructuring of Ni-P hydrogen evolution catalysts on silicon photocathodes, leading to enhanced transmission of light to the semiconductor substrate. Furthermore, Y_2SiO_5 protective layers were shown to mitigate the corrosion of Si photocathodes in alkaline environments, an electrochemical environment known to be destructive towards silicon.

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Chapter 1:

Introduction

1.1 Hydrogen as an Energy Storage Chemical

Rising global mean temperature spurred by the increasing concentration of atmospheric CO₂ will cause substantial negative changes to the global ecosystem, economy, and human civilization in ways that are complicated, non-linear, not entirely predictable, and not necessarily reversible.¹⁻³ Mitigating the greatest impacts of anthropogenic climate change will likely necessitate a rapid transition to a net-zero carbon emission system, requiring coordinated international efforts to shift the global economy in nearly all sectors including energy, industrial production, transportation, and agriculture.⁴⁻⁵ The requirement to develop technical solutions for the reduction of global CO₂ emissions has thus sparked widespread interest in the field of energy generation, both in academic and in industrial settings.

The prevalence of renewable energy alternatives to fossil fuels has been increasing for decades, and currently ~20% of domestic electricity generation comes from renewable sources, doubled from 9% in 2000.⁶ Part of this increase in renewables utilization has been driven by the steady decline in the cost of solar photovoltaics, which have dropped from \$76.67/watt in 1977 to <\$0.30/watt in 2020.⁷⁻⁸ Accordingly, solar PV is expected to make up over half of the new U.S. electricity generating capacity in 2023.⁹ In the same timeframe, utilization of coal in the U.S. has been cut by half, with new generation from natural gas making up most of that balance.⁶

However, the energy generated by renewable sources can fluctuate massively throughout the day and/or year, as well as vary on the same calendar day between successive years.¹⁰ Inconsistencies in the availability of renewable energy makes designing a net zero-carbon,

renewables-based energy system difficult because energy storage is required to smooth out intermittencies in order to meet system reliability standards. In fossil-fuel-based energy systems, inconsistencies and intermittencies caused by disruptions of supply chains or seasonal variations in fossil fuels production can be smoothed out by storing excess energy in the form of chemical fuels, i.e., a pile of coal next to a coal-fired power plant, which remains stable on geologic timescales. For renewable energy sources, long-duration storage is not as straightforward.

In recent years, advancements in the field of battery science, as well as cost decreases associated with economies-of-scale, have caused the price of lithium-ion batteries to decline from \$5000-7000/kWh in the early 1990s to \$181/kWh in 2018.¹¹ Compared to conventional lead-acid batteries, Li-ion batteries have both a volumetric and gravimetric energy density that is ~5-10× higher, which has allowed for Li-ion batteries to become deeply commercialized across many industries, from consumer electronics to electric vehicles. When charged with renewable-derived electricity, chemical batteries could seemingly be utilized as a green energy storage technology. However, the energy density of chemical fuels such as hydrogen, gasoline, methane, ammonia, and diesel still exceed the energy density of batteries by orders of magnitude (~0.3-0.4 MJ/L vs. 5-40 MJ/L).⁴ For further comparison, a gallon of gasoline contains 33.4 kWh, which (assuming \$3.5/gallon) gives an energy storage cost of ~\$0.11/kWh.

Alternatively, renewably generated electricity can be utilized to drive electrochemical water splitting, a process which generates hydrogen fuel from water. If the electrochemically generated hydrogen can be stored for later use, then a hydrogen fuel cell or turbine can be used to convert the hydrogen back into electricity, a process known as power-to-gas-to-power (PGP). Computational modeling of variable renewable electricity systems has shown that batteries and PGP lie at fundamentally different sides of the energy storage spectrum when comparing capital costs of power capacity (\$/kW) and energy capacity (\$/kWh).¹² Batteries, which have high energycapacity costs and low power-capacity costs, are well suited to smooth short-term intermittencies of renewable energy systems, such as daily charging-discharging cycles to match available sunlight, a situation when the total amount of energy stored is relatively low. As opposed to batteries, PGP has a low energy-capacity cost and high power-capacity cost due to the ease of storing a chemical fuel and the expense of electrolyzers/fuel cells, respectively. Therefore, PGP may serve as a better energy storage method for smoothing out seasonal variations of renewable energy generation.

Aside from potential use as a grid-stale long-duration energy storage chemical, hydrogen is currently one of the most important feedstock chemicals globally, with ~95 million tonnes (Mt) used yearly for refining, ammonia synthesis, methanol synthesis, and steel manufacturing, among others.¹³ A vast majority of hydrogen produced today (~95%) comes from fossil-fuel derived sources, such as during the steam methane reforming and water gas shift reactions, where CH₄, H₂O, and CO are thermochemically decomposed into hydrogen with CO₂ as a byproduct. Due to the stoichiometry of the reactions, as well as the thermal energy required to run the reactions, approximately 10 g of CO₂ are released for every 1 g of H₂.¹⁴ In total, this equates to just under 1 Gt of annual CO₂ emissions associated with hydrogen production, which is 2.5-3% of the total global CO₂ emissions of 34-37 Gt CO₂.⁴ Therefore, even if hydrogen is never utilized as a grid-scale long-duration energy storage chemical, decarbonizing the current global H₂ supply would have a substantial impact on reducing global CO₂ emissions.

1.2 Electrochemical Water Splitting

"Green" hydrogen can be generated through the electrolysis of water — also known as electrochemical water splitting — driven by electricity generated from renewable sources. In electrochemical water splitting, two electrodes are placed in contact with an aqueous electrolyte, and a voltage sufficient to cause water to split into its elemental components (hydrogen (H₂) and oxygen (O₂)) is applied across the electrodes. The overall water-splitting reaction is the sum of a reduction half-reaction and an oxidation half-reaction that occur at the cathode and anode, respectively. Equation 1 shows the water-reduction half-reaction, frequently called the hydrogen-evolution reaction (HER), in an acidic electrolyte. Equation 2 shows the water-oxidation half-reaction half-reaction and acidic electrolyte. Equation 3 shows the net reaction of Eq. 1 and Eq. 2, which is the overall water-splitting reaction.

$$2H^{+} + 2e^{-} \rightarrow H_{2}$$
(1)

$$H_{2}O \rightarrow 2H^{+} + 2e^{-} + \frac{1}{2}O_{2}$$
(2)

$$H_{2}O \rightarrow H_{2} + \frac{1}{2}O_{2}$$
(3)

The electrons travel in an external circuit from the anode to the cathode, while protons migrate through solution from the anode to the cathode, maintaining charge neutrality. Similar reactions exist for water splitting in alkaline environments, where hydroxide is the relevant ion instead of protons. A schematic of a simplified water-splitting cell is shown in Scheme 1-1.



Scheme 1-1. Schematic of a water-splitting cell, showing a cathode (left) and an anode (right) separated by a gasimpermeable ion-exchange membrane (middle). The brown circles represent catalysts for either water reduction (cathode) or water oxidation (anode).

By definition, in water splitting the generation of H_2 and O_2 are coupled directly, meaning that H_2 and O_2 are produced simultaneously at the same current and in a strictly defined stoichiometric ratio of 2:1. To avoid generating an explosive mixture of $H_2(g)$ and $O_2(g)$ during electrochemical water splitting, the anode and cathode are separated by an ion-exchange membrane or by an ion-permeable separator, such as ceramic or metal-oxide diaphragms.¹⁵

Given the thermodynamics of water splitting (1.23 V at 25 °C and 1 atm), and currentdensity-dependent losses due to catalytic overpotentials and cell resistances, electrolysis at 25 °C generally requires \geq 1.7 V in practice. Reducing voltage losses from cell resistance can be achieved by modifying the design of device components and operating parameters, such as improving gasdiffusion electrodes, modifying the flow of electrolyze through the device, changing the composition or thickness of the ion-exchange membrane, or any number of other engineering practices. Catalytic activation loses can be reduced by optimizing the anode and cathode, namely by coating them with materials that are catalytically active towards OER or HER, respectively. The specific choice of materials for electrochemical catalysts in water splitting strongly depends on the type of electrolyzer being used.

In industrial applications, the most widely used technologies are alkaline water electrolyzers (AWE) and proton exchange membrane (PEM) electrolyzers.¹⁶ AWEs have been utilized to generate hydrogen from water since the 1800s and are considered to be industrially mature. AWEs operate in strong alkaline electrolytes, such as KOH and NaOH, and are therefore optimized around materials that are stable in high-pH environments. Due to relatively high resistances inherent in the materials traditionally used in AWEs, such as thick separators, the operating current density of AWEs is restricted to lower values in the range of $0.2 - 0.4 \text{ A/cm}^2$, which substantially increases the footprint of industrial AWEs.¹⁷⁻¹⁸ Although new components and designs are being investigated to overcome these limitations and thereby increase the operational current density of AWEs, they are not yet considered industrially mature. PEM electrolyzers, a technology first developed in the 1960s to overcome issues associated with AWEs, utilize acidic conditions in an integrated polymer electrolyte to enable much higher current densities of 1-10 A/cm², depending on the specific device.¹⁶⁻¹⁷ Unlike AWEs, which use cheap Ni-based electrocatalysts, efficient operation of PEMs presently requires the use of expensive platinumgroup elements.¹⁹⁻²⁰

In industrial applications, PEM electrolyzers utilize Pt and Ir as the HER and OER catalysts, respectively. Both materials are highly stable and exceptionally efficient at catalyzing their respective reduction and oxidation half reactions. However, both materials are expensive and rare. Ir poses a particular bottleneck in scale-up of PEM electrolyzers because it is the rarest naturally occurring, non-radioactive element on earth, and is presently only mined as a byproduct of Pt

mining.²¹ Meeting the current industrial demand for H_2 with PEM electrolyzers would require diverting 10% of global iridium production for the next 200 years. Finding a suitable earth-abundant material to replace iridium in this application is an important component of this thesis work.

1.3 Decoupled or Chemical Water Splitting

Decoupled or chemical water splitting has potential to provide a flexible alternative to conventional electrolytic water splitting for the generation of hydrogen.²²⁻²⁸ In decoupled electrochemical water splitting, the HER is coupled to an oxidation half-reaction of a redox mediator (M⁻), while the OER is coupled to a reduction half-reaction of M:

$$2H^{+} + 2e^{-} \rightleftharpoons H_{2} \qquad 2M + 2e^{-} \rightleftharpoons 2M^{-} \\ 2M^{-} \rightleftharpoons 2M + 2e^{-} \qquad H_{2} 0 \rightleftharpoons 2H^{+} + 2e^{-} + \frac{1}{2}O_{2} \\ 2H^{+} + 2M^{-} \rightarrow H_{2} + 2M \qquad (4a) \qquad 2M + H_{2}O \rightarrow 2M^{-} + 2H^{+} + \frac{1}{2}O_{2} \qquad (5a)$$

The net reaction (sum of Eq. 4a and Eq. 5a) is equivalent to the water-splitting reaction (Eq. 3), and H₂ and O₂ are collected as outputs. The mediator is cycled back and forth through oxidation states in a manner akin to either a redox-flow battery (RFB) or a solid-state battery, depending on whether the mediator is in a liquid or solid phase. In both electrochemical water splitting and decoupled electrochemical water splitting, the only system inputs are water and electrical power, and the only outputs are H₂ and O₂. As written, Eq. 4a and Eq. 5a are not individually in proton balance, meaning that the pH will change if Eq. 4a is operated without Eq. 5a (and vice-versa). However, since pH is on a log scale and can be determined largely by the electrolyte, the actual pH change during independent operation of the decoupled cells depends on both the initial pH of the electrolyte and the current passed during decoupled operation. Eq. 4a and Eq. 5a can be modified slightly for mediators that also uptake and release protons during operation:

$$2H^{+} + 2e^{-} \rightleftharpoons H_{2} \qquad 2M^{*} + 2H^{+} + 2e^{-} \rightleftharpoons 2MH_{2} \\ 2MH_{2} \rightleftharpoons 2M^{*} + 2H^{+} + 2e^{-} \qquad H_{2}O \rightleftharpoons 2H^{+} + 2e^{-} + \frac{1}{2}O_{2} \\ 2MH_{2} \rightarrow H_{2} + 2M^{*} \qquad (4b) \qquad 2M^{*} + H_{2}O \rightarrow 2MH_{2} + \frac{1}{2}O_{2} \qquad (5b)$$

The net reaction is still equivalent to the water-splitting reaction (Eq. 3), but the system remains in proton balance. Mediators operated in alkaline environments undergo similar reactions as those shown in Eq. 4 and Eq. 5, but are balanced with hydroxide ions rather than protons.

Coupling to M allows separation of the HER and OER in time, space, or both. Purported benefits of such arrangements include (1) the removal or substitution of costly electrolyzer components, such as ion-exchange membranes and precious metal catalysts, (2) facile coupling with intermittent renewable energy sources; (3) membrane-free generation of pressurized hydrogen, and (4) mitigation of the risk of explosion that accompanies simultaneous production of H_2 and O_2 during water splitting.

M can be either a soluble redox couple, such as V^{3+}/V^{2+} or $[Fe(CN)_6]^{3-/4-}$, or a solid, such as NiOOH/Ni(OH)₂.²⁹ The phase of M affects the physical components as well as the operation of the system. Systems with a soluble redox mediator can operate under either static or flow conditions because M can be pumped between chambers. In systems with solid-state mediators, M typically is integrated with an electrode that can be moved between cells to be partnered with the HER or OER.

Depending on the choice of M, the standard potential $E^0(M^{0/-})$ may fall either inside or outside of the potential range bracketed by $E^0(H^+/H_2)$ and $E^0(O_2/H_2O)$. If $E^0(M^{0/-})$ falls between $E^0(H^+/H_2)$ and $E^0(O_2/H_2O)$, then coupling to M can reduce the maximum instantaneous power required by the system by dividing the thermodynamically required voltage for water splitting into multiple non-spontaneous steps. If $E^0(M^{0/-})$ falls outside of the range from $E^0(H^+/H_2)$ to $E^0(O_2/H_2O)$, then coupling to M can increase the thermodynamically required voltage for the first step, but the second step can proceed spontaneously without any external circuit or electrochemical cell. An example schematic of a decoupled electrolysis system with a soluble mediator with $E^{0}(M^{0/-})$ negative of $E^{0}(H^{+}/H_{2})$ is shown in Scheme 1-2.



Scheme 1-2. Schematic of a decoupled electrolysis system in which the first step A). has the electrochemical oxygen evolution reaction paired with the reduction of a mediator, and the second step B) has the mediator reacting with protons across a catalyst bed to drive chemical hydrogen evolution and the oxidation of the mediator back to its initial oxidation state. The mediator M has $E^0(M^{0/-})$ negative of $E^0(H^+/H_2)$ in this example.

1.4 Photoelectrochemical Water Splitting

Photoelectrochemical (PEC) water splitting is a proposed technology for the integration of all parts of a renewably-powered electrolyzer system into a single cheap and scalable device. In conventional electrolysis devices, an external power source, such as grid power or direct coupling to a solar panel array, is used to drive the water splitting reactions. PEC devices are the furthest extension of directly coupling to renewable power sources, where instead of powering an electrolyzer with an external solar panel array (PV+E), the semiconducting light absorbers are directly integrated into the electrochemical device. A purported benefit of component integration is a reduction in balance-of-system costs, which includes hard system costs (wiring, inverters, etc.) and soft system costs (site prep, labor, overhead, etc.), which combined account for ~30-50% of total device capital costs, depending on the specific technology.³⁰ Technoeconomic analysis of hydrogen (LCOH) of \$2-4/kg, compared to \$7-20/kg for PV+E systems, \$3-7/kg for grid-energy electrolysis systems, and \$2/kg for thermochemical steam methane reforming.³⁰⁻³³ PEC devices are being studied extensively for this reason.³⁰

A schematic of one proposed geometry for an integrated PEC device is shown in Scheme 1-3, with the electrochemical reactions balanced for an acidic electrolyte. Devices operated in alkaline electrolytes would be balanced with modified half-reactions and OH^- as the ion that migrates across the membrane separator.



Scheme 1-3. Schematic of a photoelectrochemical electrolysis device in an acidic electrolyte, shown with OER and HER catalysts, protective coatings, semiconducting light absorbers, and membrane separator.

In the shown PEC device, large band-gap n-type semiconductor microwires are situated in the upward-facing half of the cell, where they would absorb high energy photons (~1.8 eV), and allow sub-band-gap photons to travel to the bottom half of the cell, where the photons could be absorbed by the small band-gap p-type semiconductor below (~1.2 eV). Radially doped semiconductor junctions built into the microwires would drive photoexcited electrons in the top cell away from the semiconductor surface and photoexcited electrons in the bottom cell towards the semiconductor surface, in the same way that semiconductor junctions in Si photovoltaics drive charge carriers towards current collectors. Catalysts decorated on the exterior layer of the semiconductor microwires would collect these photogenerated charge carriers and drive their respective water splitting half-reactions. Electrons liberated from water in the top cell would travel down the length of the microwire and into the bottom cell, while protons liberated from the same water in the top cell would diffuse downwards and through the proton exchange membrane, completing the electrochemical circuit and maintaining charge neutrality. These protons and electrons recombine in the bottom cell to generate H₂, which subsequently could be collected as a chemical fuel.

Although the integration of multiple parts of a conventional electrolyzer into a single device may reduce system costs through the elimination of external power conversion equipment and the reduction of balance of system costs, integration adds additional complications from the complex interactions of the now coupled components.^{30-31, 34} Two notable complications for the scope of this thesis are the instability of semiconductors in aqueous environments and the opacity of metal catalysts.

1.4.1 Catalyst Integration

In light-facing devices, an apparently inherent trade-off exists between catalyst activity and light transmission. Semiconductors of interest for PEC water electrolysis (Si, GaAs, CdTe, InGaP, etc.) must be decorated with catalyst materials in order to drive either HER or OER at reasonable current densities. The conformal coating of catalytic materials on an electrode surface, such as the sputter deposition of metallic Pt onto a silicon photocathode, dramatically enhances catalytic activity at the expense of blocking incident illumination from reaching the semiconductor substrate below. Dense metallic layers less than 10 nm in thickness can parasitically absorb over half of the incoming illumination, effectively reducing the maximum achievable current density to half of the initial value.³⁵ Significant research efforts have focused on strategies to structure catalysts and light absorbers in order to break this tradeoff between activity and transmission.³⁵⁻⁴² One such

strategy, the electrodeposition of catalytic films that undergo self-structuring, is a focus of one chapter of this thesis.

1.4.2 Semiconductor Corrosion and Stability

Another barrier to implementation of PEC devices is the inherent instability of many semiconductors in aqueous environments.⁴³ For example, silicon readily etches in alkaline environments at open circuit, and GaAs is anodically stripped across a wide pH range. Research focus on semiconductor corrosion hopes to identify regions of stability, as well as specific failure mechanisms of different semiconductors.⁴⁴⁻⁴⁷

In order to combat the inherent instabilities of certain semiconductor-electrolyte combinations, protective coatings have been applied to physically isolate semiconductors from solution.^{43, 48-49} However, because no experimentally tested device is entirely imperfection-free, both intrinsically and extrinsically generated defects can lead to the eventual failure of such devices.⁵⁰ The study of such failure mechanisms, as well as the expansion of the library of stable layers for photoelectrode protection are of paramount importance for the PEC research community.

1.5 Scope of Thesis

This thesis focuses on the replacing the precious metal catalysts traditionally used for water electrolysis with earth-abundant alternatives, integrating these catalysts into (photo)(electro)chemical water electrolysis systems, and ensuring the long-term operation of such systems, when appropriate. Chapter 2 explores the use of bulk-synthesized Mn_ySb_{1-y}O_x powders as chemical water oxidation catalysts in a cerium-mediated decoupled electrolysis scheme. Chapter 3 studies the integration of Ni-P catalysts with silicon photocathodes, and how

electrodeposition conditions can impact the spontaneous formation of structures that enhance the performance of such devices. Chapter 4 investigates the protection of otherwise unstable silicon photocathodes in alkaline environments with Y_2SiO_5 protective coatings.

Chapter 2:

Powdered Mn_ySb_{1-y}O_x Catalysts for Cerium-Mediated Oxygen Evolution in Acidic Environments

2.1 Introduction

Fuel-forming processes such as hydrogen evolution, CO₂ reduction, and nitrogen fixation require water oxidation to O₂(g) to balance charge and complete the chemical reaction. State-of-the-art proton exchange membrane (PEM) electrolyzers utilize Ir oxide as the water oxidation catalyst, with substantial research focused on reducing the loading or increasing the activity of iridium for this application. Redirecting 10% of current annual global Ir extraction and production for 200 years would be required to build enough electrolyzers to meet the present-day global hydrogen demand, assuming that the extractable iridium on earth would not be fully depleted as a result of such efforts.²¹ Earth-abundant, active, and stable catalysts for electrochemical water oxidation are clearly desirable to facilitate scalable and cost-effective electrolyzers for generation of hydrogen from decarbonized electricity sources.

A variety of earth-abundant materials have been evaluated for use as catalysts for the oxygen-evolution reaction (OER) in acidic aqueous electrolytes, including CoO_x, MoS₂, cobalt-doped hematite, CN_x, Ni₂Ta, N-WC, NiS, and mixed metal-antimony oxides.⁵¹⁻⁶¹ PbO_x-based catalysts have been utilized for industrial oxidation reactions for decades, and PbO_x has been utilized as a stable support for otherwise unstable transition-metal OER catalysts in acidic environments.⁶¹⁻⁶³ Binary manganese antimony oxides (Mn_ySb_{1-y}O_x) have shown to be effective electrocatalysts for the OER in acidic environments, exhibiting stable operation for days in highly acidic solutions.^{20, 64} These binary metal oxide catalysts combine MnO_x, a highly active but unstable catalyst, with SbO_x, a highly stable material that has low catalytic activity for water

oxidation. Initial studies utilizing Mn_ySb_{1-y}O_x bonded the catalyst to conductive electrode supports by magnetron sputtering of high-purity Mn and Sb precursor metals under high vacuum conditions, whereas simpler synthetic methods, such as drop-casting from dissolved metal-antimony solutions, have been investigated recently.^{20, 52, 64} Commercial PEM electrolyzers are manufactured by suspending electrocatalyst powders in an ink that is subsequently sprayed on and/or impregnated into an ion-exchange membrane, to create a catalyst-coated membrane (CCM).⁶⁵ Thus, the development of a free-standing Mn_ySb_{1-y}O_x catalyst powder is a desirable step towards the integration of Mn_ySb_{1-y}O_x as an OER catalyst in conventional electrolyzer designs and fabrication processes.

 $Mn_ySb_{1-y}O_x$ catalyst powders may also be useful as heterogeneous catalysts for chemically driven water oxidation in a decoupled water-splitting scheme. In such systems, the water oxidation and reduction reactions are spatially and/or temporally isolated by pairing these transformations to the reversible reduction and subsequent oxidation of an intermediate redox mediator.^{22, 66-69} Precious metal catalyst beds in decoupled water splitting systems provide mass-normalized rates of hydrogen production (50 – 3,500 mmol h⁻¹ mg⁻¹) that far exceeded those in commercial PEM electrolyzers (19 mmol h⁻¹ mg⁻¹), and rates which remain competitive with more advanced research-scale PEM systems (4,500 mmol h⁻¹ mg⁻¹).⁷⁰⁻⁷³

Moreover, decoupled electrolysis systems that use beds of earth-abundant hydrogen evolution catalysts, such as Ni₂P, CoP, MoS₂, and Mo₂C, exhibit hydrogen evolution rates $(1 - 10 \text{ mmol } h^{-1} \text{ mg}^{-1})$ comparable to those of CoP in a traditional PEM design (35 mmol $h^{-1} \text{ mg}^{-1})$.^{67, 74-77} Mass-normalized rates of hydrogen production were calculated for PEM electrolyzers based on the reported mass loading of catalyst, using the highest current density reported for that loading, and assuming 100% faradaic efficiency towards hydrogen evolution. Mass-normalized rates of

hydrogen production for decoupled water splitting systems were reported directly from values in the corresponding references.^{70-71, 74-76} To date, OER catalyst beds in acidic decoupled electrolysis systems have used precious metal catalysts, such as RuO_x and IrO_x .⁶⁸ The development of Mn_ySb_{1-} _yO_x catalyst powders could thus also be beneficial to decoupled electrolysis schemes (Scheme 2-1).



Scheme 2-1. Reaction scheme demonstrating the two-step process of cerium-mediated chemical water oxidation in acidic aqueous environments in which (A) hydrogen is evolved and cerium is oxidized under the application of an external bias and (B) oxygen is evolved spontaneously over a MnySb1-yOx particle

Powdered earth-abundant (CoP, $Mn_ySb_{1-y}O_x$, etc.) catalysts in chemical electrolysis schemes are not necessarily better than utilizing precious metal (Pt, IrO_x, etc.) catalysts in conventional electrochemical electrolysis systems. Rather, earth-abundant materials have a potentially different use case and are multiple orders of magnitude more abundant and less expensive than their precious metal alternatives.

Due to the operational mode of decoupled electrolysis systems, the water splitting halfreactions can be isolated spatially, temporally, or both. Such isolation allows for the elimination of product gas crossover, the ability to work in membrane-free systems, and intrinsic safety as hydrogen and oxygen are not generated in the same location.^{70, 78} Other reported potential benefits include a lesser degree of separator degradation, the ability to flexibly pair HER or OER with other oxidation or reduction reactions, respectively, and the ease of increasing catalyst loadings in catalytic beds.^{67, 79-80}

2.2 Materials and Methods

2.2.1 Chemicals and Sample Preparation

All chemicals were commercially available and used as received. Manganese (II) acetate tetrahydrate (99.99% trace metal basis), antimony (III) oxide (nanopowder, < 250 nm), ammonium cerium (IV) nitrate (ACS reagent \geq 98.5%), iron (II) sulfate heptahydrate (ACS reagent \geq 99.0%), and methanesulfonic acid (\geq 99.5%) were obtained from Sigma Aldrich. Iridium (IV) oxide (Premion, 99.99% metals basis) was obtained from Alfa Aesar. Perchloric acid (69-72%) and sulfuric acid (TraceMetal grade, 95%) were obtained from Fischer Chemical. Acids were diluted to 1 M using 18.2 M Ω -cm resistivity water obtained from a Thermo Scientific Nanopure deionized water system.

Manganese acetate and antimony oxide powders were mixed in the desired ratio and thoroughly ground together with a mortar and pestle. The ground powder was dried in air in a ceramic crucible in a muffle furnace (Thermolyne F48020-80) for 1 h at 150 °C to remove any moisture, followed by calcination for 5 h at 750 °C with a ramp rate of 10 °C min⁻¹. The samples were ball milled for 30 min in a 20 mL agate jar with a 7.9 mm agate ball using a SPEX mini mixer/mill 5100, resulting in micron-sized agglomerates. A pellet was prepared by using a set of heated dies and a manual hydraulic press to hot press 50 mg of the sample for 10 min at 100 °C. The electrical conductivity of the material was measured using a 4-point probe on a 6 mm diameter, ~ 0.5- 1.2 mm thick hot-pressed pellet. The MnO_x catalyst was made by the same methods but without addition of any antimony oxide. Sb₂O₅ XRD and UV/Vis standards were made by annealing as-received Sb₂O₃ powder for 24 h at 425 °C in air.

2.2.2 Chemical Rate Experimental Details

For chemical rate experiments, 35-50 mg (as specified in the main text) of powdered $Mn_ySb_{1-y}O_x$ catalysts were washed in the reaction solution, dried, and added to a fresh mixture of 50 mM of cerium ammonium nitrate (CAN) in 10 mL of 1.0 M HClO₄ in a 25 mL Erlenmeyer flask. Washing the catalyst was found to slightly increase the oxygen yield and increase the reaction rate for all catalysts. The flask was sealed with a rubber septum lined with high vacuum grease. A needle with a Luer-lock attached to a polyethylene tube was inserted through the top of the septum and sealed with vacuum grease. The tubing was connected to a water-filled inverted graduated cylinder whose opening was submerged in a large beaker filled with water. Bubbles were collected in this home-made eudiometer setup, and the elapsed time and liquid volume was recorded throughout the experiments.

For experiments that required re-use of the same catalyst powder or characterization after the experiment, the reaction mixture was collected after oxygen bubble generation subsided. Powder was separated from the solution through centrifugation in an LW Scientific CXR centrifuge at 3400 rpm. When needed, this first supernatant was collected for ICP-MS analysis. Otherwise, the supernatant was discarded, fresh water was added to the wet powder, and the powder was redispersed with sonication and manual shaking. This centrifugation-washing process was repeated for one time more than necessary for the water-powder dispersion to attain neutral pH, which was at least 3 times. The wet powders were dried at 100 °C in air.

For determination of the turnover number, the solution volume was increased to 100 mL and the cerium ammonium nitrate concentration was increased to 300 mM, with otherwise identical experimental methods. To minimize evaporation during long-duration experiments, the large bottom beaker of water was covered tightly with Parafilm. To confirm that the product was

 $O_2(g)$, a fluorescent oxygen sensing probe (Ocean Insight, NeoFox with RedEye patches) was used to monitor the headspace oxygen concentration during preliminary experiments.

2.2.3 Characterization Techniques

The bulk stoichiometry, particle size, and morphology of the as-made catalysts were determined by energy-dispersive X-ray (EDX) spectroscopy and scanning electron microscopy (SEM). Both measurements were conducted in the same FEI Nova NanoSEM 450 at a working distance of 5 mm. SEM images were collected at a 5-10 kV accelerating voltage, with EDX data collected at 15 kV. EDX spectra were collected from n = 6-8 particulates for each composition, and then averaged together. The INCA software package (Oxford Instruments) was used to analyze the EDX spectra.

Powder X-ray diffraction (XRD) patterns were collected on a Bruker D2 Phaser equipped with a copper tube and a LynxEye 1-dimensional detector with a 2.3° Soller slit. Samples were prepared by filling the specimen well of a Si crystal specimen holder with dry powder. Patterns were measured using a step size of 0.01 2 θ , a variable rotation of 5.0 min⁻¹, and with X-ray generation at 30 kV voltage and 10 mA current. XRD reflection patterns were matched to database standards for Mn₂O₃ (00-001-1061), Mn₃O₄ (00-008-0017), as well as rutile MnSb₂O₆ (04-011-4962) and hexagonal MnSb₂O₆ (04-010-3922) from reference.⁶⁴

Diffuse reflectance spectroscopy (DRS) UV-vis was conducted using a Cary 5000 UV-vis-NIR with an integrating sphere. Samples of powder were rubbed onto black electrical tape, which was used to cover the sampling port in reflectance mode. Data were collected from 200-2000 nm with a step size of 0.5 nm. A linear fit of known oxide standards was used to approximate the Mn oxidation state.
X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Axis Ultra system with a base pressure of 1×10^{-9} Torr in the analysis chamber. A 150 W monochromatic Al Ka source was used to irradiate the sample with X-rays (1486.7 eV). A hemispherical analyzer oriented for detection along the sample surface normal was used for maximum depth sensitivity. The data were analyzed using CasaXPS computer software. A Shirley background was used for Mn spectra while a U 2 Tougaard background was used for Sb, O, and C spectra. All peaks were referenced to adventitious C at a binding energy of 284.8 eV.

The Mn $2p_{3/2}$ peak was fit to standards previously reported to estimate the oxidation state and the contribution of various oxidation states to the XPS peaks.⁸¹ To rigorously determine the Mn oxidation state, prior work has used high-purity standards for Mn 2p fitting as well as the Mn 3p peak and Mn 3s multiplet splitting.⁸¹⁻⁸⁸ However, Mn has multiple common oxidation states (II, III, and IV) that may coexist within a sample, complicating interpretation of the Mn XP spectra. Interpretation of the Sb XP spectrum is complicated by the overlap of the Sb 3d_{5/2} peak with the O 1s peak. However, the Sb 3d_{3/2} peak has no overlap with O. Thus, the Sb 3d_{5/2} contribution was determined by constraining the peak splitting (Δ Sb 3d = 9.38 eV), the full width at half maximum (FWHM) (equivalent for the same chemical state), and area ratio (3d_{5/2}:3d_{3/2} = 3:2) and assuming that the remaining signal was due to O.⁸⁹⁻⁹⁰

Particle size analysis was conducted by measuring the diameter of n = 500 particles at each composition from images captured via SEM at low magnification (~400x magnification). A small scoop of powder was placed onto a carbon-tape covered SEM stub. The stub was tapped, shaken, and inverted to remove the loose powder.

2.3 Results and Discussion

2.3.1 Material Characterization

 $Mn_ySb_{1-y}O_x$ particulate agglomerates were synthesized by grinding as-received $Mn(C_2H_3O_2)_2 \cdot 4H_2O$ and Sb_2O_3 powders together, calcining the mixture at 750 °C for 5 h, followed by ball milling.

Scanning electron micrographs (SEMs) of representative $Mn_ySb_{1-y}O_x$ particulates showed secondary particle diameters on the order of 10 µm (Figure 2-1a). The distribution of particle diameters for n = 500 particles of each composition showed a consistent particle size with a median diameter D_{50} around 12 µm. Elemental analysis using energy-dispersive X-ray (EDX) spectroscopy indicated that the bulk catalyst composition closely matched the nominal catalyst composition. The electrical conductivity obtained by four-point probe measurements on hotpressed powder samples decreased by over two orders of magnitude as the Mn composition (Mn_y) decreased from $Mn_{0.8}Sb_{0.2}O_x$ (Mn_{0.8}) to $Mn_{0.2}Sb_{0.8}O_x$ (Mn_{0.2}) (Table 2-1, Figure 2-15, Table 2-4).

Table 2-1	. Bulk	elemental	composition	(from	EDX),	average	particle	diameter	(from	SEM	images),	and	bulk
conductiv	ity of a	s-prepared	catalyst powd	ers.									

Catalyst	Ratio of Mn:	Median Diameter,	Conductivity	
	Mn/(Mn+Sb)	$D_{50}(\mu m)$	$(S/m \times 10^{6})$	
$Mn_{0.8}Sb_{0.2}O_x$	0.83 ± 0.02	11.4	2.65	
$Mn_{0.6}Sb_{0.4}O_x$	0.64 ± 0.01	11.8	1.12	
$Mn_{0.4}Sb_{0.6}O_x$	0.43 ± 0.01	12.7	0.05	
$Mn_{0.2}Sb_{0.8}O_x$	0.20 ± 0.02	11.8	0.01	



Figure 2-1. (A) Representative SEM image of Mn0.8Sb0.2Ox particles. (B) XRD patterns of the family of annealed MnySb1-yOx powders, with relevant reflections of rutile MnSb2Ox (red star), hexagonal MnSb2Ox (purple circle), Mn3O4 (black square), Sb2O5 (blue +), and Mn2O3 (green x). (C) Effective oxidation state of Mn in the MnySb1yOx powders as determined by XPS (red) and DRS (blue).

X-ray diffraction (XRD) patterns collected from annealed $Mn_ySb_{1-y}O_x$ powders from $Mn_{0,2}$ to $Mn_{0.8}$ showed reflections at $2\theta \approx 27, 35, 38, 53, and 56$ degrees (Figure 2-1b), indicative of a rutile $MnSb_2O_6$.^{20, 64, 91} These reflections have been observed previously in rutile $Mn_ySb_{1-y}O_x$ alloys with the reflections generally shifting to slightly higher values of 2θ as Mn_y is increased.⁶⁴ These rutile reflections were substantially smaller in magnitude for the $Mn_{0,2}$ sample. Additional reflections indicative of a hexagonal MnSb₂O₆ were present for $Mn_y \leq 0.4$, consistent with previous characterization.⁶⁴ Reflections indicative of both Mn₂O₃ and Mn₃O₄ were present for Mn_{0.8} and became less prominent as Mn_v decreased. The potential impact of these MnO_x impurity phases is discussed below. Reflections characteristic of Sb oxides began to appear at $Mn_y \le 0.6$ and were most prominent for Mn_{0.2}. The exact positions of the rutile MnSb₂O₆ reflections have been previously reported to vary across the compositional space. As the Mn composition decreased from $Mn_v = 0.8$ to 0.2, the positions of the [101], [110], [211], and [220] peaks have been reported to shift from 36.2° to 34.8°, 27.3° to 26.7°, 54.0° to 52.5°, and 56.6° to 55.2°, respectively. These shifts in the $Mn_ySb_{1-y}O_x$ reflections were also observed herein across the compositional space of the powdered Mn_ySb_{1-y}O_x catalysts. The identity of the homemade Mn₂O₃ sample was confirmed with XRD analysis, which showed a material match to the database Mn_2O_3 sample.

X-ray photoelectron (XP) spectra of the Mn 2p region indicated that Mn^{3+} was the primary surface oxidation state in the rest state of the catalysts, with contributions from other Mn oxidation states increasing as Mn_y decreased (Figure 2-2). The Mn_{0.8} and Mn_{0.6} samples showed mutually similar XPS emissions, with >80% of the weighted peak area attributable to Mn³⁺. The effective Mn oxidation state decreased monotonically from +2.9 to +2.6 as the Mn content decreased from Mn_{0.8} to Mn_{0.2}. Additional elaboration of the methods and inherent uncertainties associated with estimating the oxidation state of transition metals from XP spectra are presented in Figure 2-16 and Figure 2-17.



 $\label{eq:Figure 2-2. XP spectra of the Mn 2p orbitals of the range of Mn_ySb_{1-y}O_x \mbox{ catalyst families, including peak fitting packets of Mn into Mn^{2+} (blue), Mn^{3+} (yellow), and Mn^{4+} (green).}$

Diffuse reflectance UV/visible (DRS) spectra were used to determine the effective oxidation state of Mn in each sample, determined utilizing linear combination methods.⁹² Kubelka-Munk transforms of diffuse reflection data of the range of Mn_ySb_{1-y}O_x catalyst powders are shown in Figure 2-3. The K-M transform is of the form: $KM(\lambda) = \frac{(1-R(\lambda))^2}{2*R(\lambda)}$. The K-M transforms of standard powders of known composition were linearly scaled and summed together to determine a best fit for each of the $Mn_vSb_{1-v}O_x$ spectra in Figure 2-3. The fit was determined by varying the scaling factor of each of the oxide standards and minimizing the sum of squared error between the fit and the actual K-M transform data. The fit was only considered between 250-1200 nm. In each, the fit is shown in dotted black lines, and the sample spectrum is shown in green. No material exhibited the strong peak at ~600 nm so the standard for MnO was excluded from the fit to avoid over-parameterization. This process did not meaningfully alter the final oxidation state calculation. The Mn oxidation state was determined to be (with MnO vs. without MnO): $Mn_{0.8}$ (3.20 vs. 3.21), $Mn_{0.6}$ (3.19 vs 3.22), $Mn_{0.4}$ (2.97 vs 3.03), and $Mn_{0.2}$ (2.64 vs 2.67). The resulting estimated values for the Mn oxidation state were in good agreement with the surface oxidation state determined by XPS (Figure 2-1c).



 $\label{eq:starsest} \begin{array}{l} \mbox{Figure 2-3. DRS data fit for (A) $Mn_{0.8}Sb_{0.2}O_x$ catalyst, (B) $Mn_{0.6}Sb_{0.4}O_x$ catalyst, (C) $Mn_{0.4}Sb_{0.6}O_x$ catalyst, and (D) $Mn_{0.2}Sb_{0.8}O_x$ catalyst. \\ \end{array}$

2.3.2 Reaction Rate Experiments

Chemical oxygen-evolution experiments, in which ~35 mg of $Mn_ySb_{1-y}O_x$ catalyst powder was added to a stirred 10 mL solution of 50 mM Ce(IV) in 1 M HClO₄ (Scheme 2-1b), showed the generation of oxygen gas over time (Figure 2-4). The rate of $O_2(g)$ production from each catalyst followed first-order kinetics (Figure 2-18 and Figure 2-19), and the rate of reaction increased as the Mn composition increased.



Figure 2-4. Oxygen evolution time series data for Mn_ySb_{1-y}O_x catalysts in perchloric acid. Squares, diamonds, and triangles represent data from triplicate trials, with the colored areas showing one standard deviation of a first-order kinetic fit to the data (Figure 2-18).

For catalysts with $Mn_y \ge 0.4$, the average amount of oxygen generated upon reaction completion was 3.0 ± 0.13 mL, and the theoretically expected volume for 100% yield is 3.06 mL. Reaction completion for the $Mn_{0.4}$ catalyst required ~24 h. The 0.45 mL of oxygen generated after >40 h using the $Mn_{0.2}$ catalyst was substantially lower than the theoretically expected value. Fluorometric analysis indicated that the liberated gas was $O_2(g)$. After the catalysts with $Mn_y \ge 0.4$ were removed from the HClO₄/Ce⁴⁺ solution, the yellow color of Ce⁴⁺ was visually absent in the solution. The volume of gas collected, fluorometric oxygen detection, and color change of the solution collectively show that the $Mn_ySb_{1-y}O_x$ catalysts facilitate the generation of $O_2(g)$ from water with close to 100% yield and selectivity via the reduction of Ce⁴⁺ to Ce³⁺. As the relative fraction of Mn in the catalyst increased from $Mn_{0.2}$ to $Mn_{0.8}$, the initial oxygen generation rate increased by a factor of nearly 400, from 4.4×10^{-4} to 1.7×10^{-1} mL mg⁻¹ h⁻¹ (Figure 2-5). For comparison, the reaction rate over a homemade Mn_2O_3 sample is shown at $Mn_y = 1$ as 1.1×10^{-1} mL mg⁻¹ h⁻¹. The observed reaction rate over Mn_2O_3 is likely lower than that of $Mn_{0.8}Sb_{0.2}O_x$ due to the rapid deactivation of pure Mn oxide catalysts under these conditions.⁶⁴ Figure 3 also shows the electrochemical current density obtained from electrodes coated with sputtered $Mn_ySb_{1-y}O_x$ catalysts biased at 1.79 V vs. the reversible hydrogen electrode (RHE) (black, from ref. ⁶⁴). The close agreement between the rate data indicates that this family of $Mn_ySb_{1-y}O_x$ powders are functionally similar to previously reported $Mn_ySb_{1-y}O_x$ catalysts used on planar electrodes.



Figure 2-5. Reaction rate summary for powdered $Mn_ySb_{1-y}O_x$ catalysts (blue, left y-axis) and the current density during previous electrochemical evaluation of sputtered $Mn_ySb_{1-y}O_x$ catalysts recorded at 1.79 V vs RHE during cyclic voltammetry experiments in 1.0 M H₂SO₄ (black line, right y-axis) (Adapted from reference⁶⁴. Copyright 2018 American Chemical Society)

As Mn_v increased from 0.2 to 0.8, the initial reaction rate increased (Figure 2-5) and the Mn oxidation state increased to Mn^{3+} (Figure 2-1c, Figure 2-17). The rate of oxygen generation was also normalized by the amount of Mn³⁺ present in the near-surface region of the catalyst particles, which resulted in a mutually consistent estimate of the Mn-normalized oxygen generation behavior for the $Mn_v \ge 0.4$ samples (Figure 2-6), and the ratio of the initial reaction rate (r_y) for $r_{0.4}$: $r_{0.6}$: $r_{0.8}$ shifted from 1 : 2.1 : 9.3 to 1 : 1.3 : 2.1. Figure 2-4 shows the oxygen generated over time when 35 mg of each catalyst from the family of Mn_vSb_{1-v}O_x catalysts was used. However, the bulk Mn composition (Mn_v) was different for each of these catalysts, as was the oxidation state. Utilizing the bulk composition determined by EDX and the total mass of catalyst, the total mass of purely Mn in the catalyst was calculated. XPS was then utilized to determine the near-surface oxidation state of Mn in the material. This analysis indicated that in the Mn_{0.8}, Mn_{0.6}, and $Mn_{0.4}$ catalysts, the atomic proportion of near-surface Mn in the Mn^{3+} oxidation state was 81%, 80%, and 42%, respectively. The near-surface oxidation state of Mn in the catalyst powders was considered to be the critical parameter because the chemical OER occurs across the surface of the catalyst, not within the inaccessible bulk of the non-porous catalyst material. An arbitrary length can be selected for the thickness of the "near-surface" region to determine the total amount (mass or moles) of Mn^{3+} present across the surface of the particles. This length is arbitrary because it is the same estimation for each catalyst composition and will therefore cancel out when reactionrate-ratios are being computed. Although some Mn leaching occurred during the oxygen evolution experiments (Figure 4b), the amount is small compared to the total mass of catalyst (<0.5%). When the oxygen generation rate was normalized by the mass of Mn³⁺, the resulting data for samples with $0.4 \le Mn_y \le 0.8$ provided a self-consistent estimate of the initial reaction rate for oxygen generation per Mn^{3+} site (Figure 2-6).



Figure 2-6. (A) Oxygen evolution data from Figure 2 during the first 100 minutes. (B) Data from (A) normalized by the Mn^{3+} in each catalyst powder for $Mn_ySb_{1-y}O_x$ powders for $Mn_y = 0.8$ (blue), 0.6 (green), and 0.4 (black).

These observations are consistent with previous results for OER catalysis for the $Mn_ySb_{1-}yO_x$ family of compounds, which demonstrated that the ex-situ stabilization of the Mn^{3+} oxidation state led to a catalyst with more activity towards the OER.⁶⁴ This behavior was directly demonstrated utilizing chemical OER experiments with various Mn oxides as catalysts (Figure 2-7). The same rate experiments (10 mL of 50 mM Ce⁴⁺ in 1 M HClO₄) were conducted for a series of MnO_x catalysts consisting of MnO, Mn₂O₃, and MnO₂, which are oxides of Mn²⁺, Mn³⁺, and Mn⁴⁺, respectively. Figure 2-7 shows the oxygen generation data over time. The process consisted

of duplicate trials for each of the oxide powders. For each catalyst, the first trial is shown as a circle and the second trial is shown as a square of the same color. The MnO catalyst released a substantial volume of gas (~0.1 mL) immediately upon addition to the reaction solution during both trials. The initial evolved gas data point was removed during the analysis to accurately fit a rate approximation to the whole data set. For each trial, the linearization of the concentration vs. time data was used to determine a slope. The line of best fit is shown in dotted black for each data set in Figure S17, while the solid black line is the average of the two fits.



Figure 2-7. O_2 generation vs. time data for Mn oxide catalysts, with two trials shown as squares and circles. Individual 1st order kinetic fits are shown as dotted black lines, with the average shown as the solid black lines.

The rate of oxygen evolution over Mn_2O_3 (Mn^{3+}) was 17 and 29 times higher, respectively, than the rate over MnO_2 (Mn^{4+}) and MnO (Mn^{2+}), when normalized for the mass of Mn in the catalyst. The MnO_2 and MnO catalysts had low oxygen yields and produced only ~1 mL of O_2 after 24 hours. In both electrochemical and photochemical applications, catalysts with an ex-situ oxidation state comprised of Mn^{3+} oxides (Mn_2O_3) have been shown to be more active towards the OER than either $Mn^{2+/3+}$ oxides (Mn_3O_4) or Mn^{4+} oxides (MnO_2).⁹³⁻⁹⁴ In-situ studies of Mn oxide catalysts have demonstrated that the oxidation state may be higher for the active phase during catalyst operation than in the rest phase.⁹⁵ No clear correlation was observed between the rate of reaction and the conductivity of the particles (Figure 2-15).

2.3.3 Extended Duration Stability Experiments

Extended-duration stability of the $Mn_ySb_{1-y}O_x$ and homemade Mn_2O_3 catalysts was assessed by using larger reaction volumes (100 mL), higher Ce⁴⁺ concentrations (300 mM), and low amounts of catalyst (~2 mg). The turnover number (TON) in these experiments is the molar ratio of O₂(g) generated relative to the Mn in the catalyst powder (Figure 2-8a). Inductively coupled plasma mass spectrometry (ICP-MS) was used to quantify the mass of Mn lost by the catalytic powders after multiple subsequent uses (10 mL of 50 mM Ce(IV) in 1 M HClO₄) (Figure 2-8b).



Figure 2-8. (A) TON measurements of $Mn_ySb_{1-y}O_x$ catalysts from $Mn_y = 0.6$ to 1.0 in 100 mL of 300 mM Ce⁴⁺ in 1 M HClO₄ using ~2 mg of catalyst. (B) Concentration of Mn present in the reaction solution after complete reduction of 50 mM Ce⁴⁺ in 10 mL of in 1 M HClO₄. Each point in a series represents the Mn concentration after a subsequent run reusing the same catalyst powder in a fresh reaction mixture.

After 360 h, the TON of the $Mn_{0.6}$ and $Mn_{0.8}$ catalysts were 52 and 30, respectively. The homemade Mn_2O_3 catalyst showed a TON of 7 after ~100 h, after which no further oxygen generation was

observed. This same set of experiments was also conducted in smaller volumes (50 mL) of solution in conjunction with lower Ce⁴⁺concentrations (100 mM), yielding TONs for the $Mn_{0.6}$, $Mn_{0.8}$, and $Mn_{1.0}$ catalysts of 26, 22, and 3, respectively. The increased TON of the $Mn_{0.6}$ catalyst relative to the $Mn_{0.8}$ and $Mn_{1.0}$ catalysts demonstrates the known stabilizing effect of the addition of Sb to MnO_x catalysts.

Previous demonstrations of non-precious metal catalysts for the chemical hydrogen evolution reaction (HER) utilizing various mediators have shown TONs in the same range as the catalysts reported here.⁶⁷ Certain bulk Ni₅P₄, Mo₂C, MoS₂, and Ni₂P particulate catalysts showed TONs of ~2-4.⁷⁴ Other materials, including structured Ni₂P, CoP, and Mo₂C exhibited TONs from 40-150.⁷⁴⁻⁷⁶ However, obtaining a high TON was not the primary focus of those investigations. Showing similar TONs to HER catalysts is notable as the HER is an easier, more facile reaction to drive compared to the OER (2 electron vs 4 electron). Overpotentials required to drive HER in electrochemical systems over these earth-abundant catalysts (NiP, CoP, MoS₂, etc.) (~150-250 mV) are much lower than those required over Mn_ySb_{1-y}O_x catalysts (~550-750 mV). This puts OER catalysis at an inherent disadvantage when directly comparing both rate and TON, yet the TONs achieved herein are still well within the middle to upper range of reported values for such systems.

In these TON experiments, the reaction rate and the catalyst stability are linked in a more complicated way than in the short-term reaction rate experiments, so a direct comparison between the two is difficult. However, when calculating the volumetric initial rate of reaction for the TON experiments, the rates are comparable to those in Figure 2-5 ($\sim 0.05 - 0.1$ mL/h mg). Obtaining enough data points to obtain an estimate for the initial reaction rate requires approximately a day

of run-time, which seems to be enough time for the $Mn_ySb_{1-y}O_x$ catalysts to start losing some activity.

In the corrosion experiments, the Mn_2O_3 showed monotonically increased corrosion of Mn after each cycle, whereas the catalysts with $Mn_{0.6}$ and $Mn_{0.8}$ showed monotonic decreases in Mn corrosion after each experiment. The diverging corrosion behavior suggests that the Sb provides a stabilizing effect on the Mn in the catalyst and inhibits corrosion. Additional reaction rate data and characterization of re-used catalyst powders indicated stable catalytic performance, decreased presence of impurity Mn_2O_3 and Mn_3O_4 phases, and consistent atomic composition over multiple catalytic cycles at experimental time scales of ~2 h (Figure 2-9 – Figure 2-13). Taken together, the TON and corrosion behavior of the antimonate catalysts indicate that the presence of Sb inhibits the corrosion of Mn, while also enabling the remaining Mn to retain catalytic activity.

Impurity Mn_2O_3 and Mn_3O_4 phases that could potentially catalyze the OER were observed in the XRD analysis of $Mn_ySb_{1-y}O_x$ samples with $Mn_y \ge 0.6$. In electrochemical experiments, the overpotential without IR compensation at 5 mA/cm² in 1 M H₂SO₄ was the same for pure Mn_2O_3 and $Mn_{0.7}Sb_{0.3}O_x$.⁶⁴ However, the pure Mn_2O_3 deactivated rapidly, and the current density at 1.8 V vs. RHE decreased by at least an order of magnitude after 40 min of electrochemical cycling at low current densities.

In this report, the rate of chemical oxygen evolution over a pure homemade Mn_2O_3 sample was lower than that of $Mn_{0.8}Sb_{0.2}O_x$ and was marginally higher than the rate over $Mn_{0.6}Sb_{0.4}O_x$. The same mass of catalyst powder was used in each experiment (~35 mg), so the total mass of the catalytic center (Mn) present in the powders was substantially larger for the experiments that used pure Mn_2O_3 than for the $Mn_ySb_{1-y}O_x$ catalysts. Hence, over the timescale required to determine an initial reaction rate for the chemical oxygen evolution reaction (~30-60 minutes), the pure Mn

oxides were less active than the manganese antimonate catalysts. The turnover number measurements and the Mn corrosion comparison between powdered Mn_2O_3 and $Mn_ySb_{1-y}O_x$ catalysts (Figure 4) showed that the pure Mn oxides were substantially less active and stable over sustained chemical oxygen evolution experiments than the $Mn_ySb_{1-y}O_x$ catalysts.

 $Mn_{0.8}Sb_{0.2}O_x$ catalyst powders were collected and re-used multiple times in successive oxygen generation experiments under the same reaction conditions in 10 mL of 50 mM Ce⁴⁺ in 1.0 M HClO₄ (Figure 2-9), and the used powders were characterized by XRD (Figure 2-10).





Figure 2-10. XRD patterns of $Mn_{0.8}Sb_{0.2}O_x$ catalysts after multiple successive experiments in 10 mL of 50 mM Ce⁴⁺ in 1.0 M HClO₄. $Mn_ySb_{1-y}O_x$ indicated by vertical dashed lines.

The rate of oxygen generation increased slightly through multiple re-uses of the $Mn_{0.8}Sb_{0.2}O_x$ catalyst powder, whereas reflections indicative of MnO_x impurities decreased in intensity, specifically around $2\theta \approx 30$, 33, 36, 45, 51, 59 degrees, as indicated by the red circles.

 $Mn_{0.6}Sb_{0.4}O_x$ catalyst powders were also collected and re-used multiple times in successive oxygen generation experiments under the same reaction conditions in 10 mL of 50 mM Ce⁴⁺ in 1.0 M HClO₄ (Figure 2-11), and the used powders were characterized by XRD (Figure 2-12).



Figure 2-11. Oxygen generated over time over $Mn_{0.6}Sb_{0.4}O_x$ catalyst through successive catalytic cycling in 10 mL of 50 mM Ce⁴⁺ in 1.0 M HClO₄.



Figure 2-12. XRD patterns of Mn_{0.6}Sb_{0.4}O_x catalysts after multiple successive experiments in 10 mL of 50 mM Ce⁴⁺ in 1.0 M HClO₄. Mn_ySb_{1-y}O_x indicated by vertical dashed lines.

The rate of oxygen generation increased through subsequent reuses of the $Mn_{0.6}Sb_{0.4}O_x$ catalyst powder material, whereas reflections indicative of MnO_x impurities decreased substantially in intensity, specifically around $2\theta \approx 30$, 33, 36, 51, and 59 degrees, as indicated by the red circles. The increase in the rate of oxygen generation as the presence of Mn_2O_3 and Mn_3O_4 impurity phases decreased provides strong evidence that the impurity phases do not substantially contribute to the rate of oxygen generation for these materials at short timescales.

EDX measurements of spent $Mn_ySb_{1-y}O_x$ catalysts after successive experiments indicated that the atomic composition Mn/(Mn+Sb) remained consistent over multiple catalytic cycles (Figure 2-13).



Figure 2-13. Bulk Mn composition of catalyst powders after successive catalytic cycling in 10 mL of 50 mM Ce^{4+} in 1.0 M HClO4, with error bars representing standard deviations between the measured samples (n = 6).

2.3.4 Utilization of Different Aqueous Environments

To further investigate the chemical oxygen-evolution behavior of the $Mn_ySb_{1-y}O_x$ family of catalysts, the formal potential of the $Ce^{4+/3+}$ redox couple was varied by changing the acid in the aqueous electrolyte. The formal potential of the $Ce^{4+/3+}$ redox couple is strongly dependent on the choice of acid, and varies from 1.3 V vs. the potential of the standard hydrogen electrode (SHE) in HCl to 1.7 V vs. SHE in HClO₄.^{68, 96} Accordingly, the redox potential of a 1 mM Ce³⁺/1 mM Ce⁴⁺ mixture in 1 M HClO₄, 1 M H₂SO₄, and a 1:1 mix of 1 M H₂SO₄ and 1 M methanesulfonic acid (MSA), was determined by cyclic voltammetry (Figure 2-14) to be 1.68 V, 1.46 V, and 1.51 V vs. RHE, respectively.

The potential of the Ce^{4+/3+} reduction/oxidation reactions was determined by voltammetry in a stirred, round-bottom 3-neck flask containing 40 mL of electrolyte (1 M acid), 50 mM Ce⁴⁺ (from ammonium cerium (IV) nitrate) and 50 mM Ce³⁺ (from cerium(III) carbonate). The working electrode was a polished Pt disk (3 mm², polished with MicroPolish Powder – 0.3 μ m), the reference electrode was a SCE, and the counter electrode was a graphite rod. Scans were collected at 30 mV s⁻¹, and the redox potential of the couple was the x-intercept for each experiment. These values were measured as 1.46, 1.51, and 1.68 V vs RHE for H₂SO₄, MSA/H₂SO₄, and HClO₄, respectively.



Figure 2-14. Cyclic voltammetry of 50 mM/50 mM mixture of Ce(III/IV) in stirred solutions of various acidic electrolytes.

Chemical oxygen evolution experiments in the 1 M H₂SO₄/MSA mixture showed a ~50fold decrease in the rate of oxygen evolution relative to the rate in perchloric acid (Table 2-2). This difference in rate is consistent with the negative shift in the formal potential of the Ce^{4+/3+} redox couple in H₂SO₄/MSA and reflects a decrease in the electrochemical driving force for spontaneous oxygen generation. The Mn_ySb_{1-y}O_x catalysts did not produce O₂(g) in H₂SO₄, consistent with the observed further negative shift in the formal potential of the cerium redox couple in this solution.

Table 2-2 summarizes the relevant rate data for the $Mn_ySb_{1-y}O_x$ catalysts in HClO₄ and in a H₂SO₄/MSA mixture, as well as the performance of a commercial IrO_x powder for comparison. The overpotential (η), i.e. the difference between the measured potential of the Ce^{4+/3+} redox couple and the thermodynamic potential of the oxygen-evolution reaction (1.23 V vs. RHE), is shown for both solutions. Given the values of the reaction rate and overpotential, the logarithm of the reaction rate can be plotted against the overpotential to produce a Tafel plot and consequently a chemical Tafel slope can be determined.

		OFD	Reaction Rate (mL h ⁻¹ mg ⁻¹)					
	Acid	η vs. OER	Mn0.8Sb0.2Ox	Mn0.6Sb0.4Ox	IrOx			
	Perchloric	0.45 V	0.165	0.078	32			
H ₂ SO ₄ +MSA		0.28 V	0.0034	0.0015	0.58			
	Reaction Rate Comparison							
	Rate Ratio							
	(HClO ₄ :	-	×48.2	×50.9	×55.4			
	[H ₂ SO ₄ +MSA])							
	Tafel Slope	-	~100 mV/dec.	~100 mV/dec.	~100 mV/dec.			

Table 2-2. The overpotential and initial oxygen evolution rates of the $Mn_{0.8}Sb_{0.2}O_x$, $Mn_{0.6}Sb_{0.4}O_x$, and IrO_x catalyst powders in HClO₄ and the H₂SO₄/MSA mixture.

The Tafel slopes were all ~100 mV/decade, in accord with a typical value of 118 mV/dec,⁹⁷ and aligning closely with the 96 \pm 7 mV/decade electrochemical Tafel slope reported for a MnSb_{1.7}O_x catalyst produced by sputter deposition.²⁰ However, these values should be considered as estimates because they were determined from only two aqueous acidic environments.

The initial rates of $O_2(g)$ generation from the $Mn_ySb_{1-y}O_x$ catalysts in HClO₄ were directly compared to the performance of the commercial IrO_x powder and were found to be 200 - 61,000 times slower than the IrO_x catalyst, depending on the composition (Table 2-3).

Catalyst Composition	Initial Reaction Rate $(mL h^{-1} mg^{-1})$	Ratio IrO _x : Mn _y Sb _{1-y} O _x
IrO _x Powder	32	—
$Mn_{0.8}Sb_{0.2}O_x$	0.165	×194
$Mn_{0.6}Sb_{0.4}O_x$	0.078	×411
$Mn_{0.4}Sb_{0.6}O_x$	0.018	×1,800
$Mn_{0.2}Sb_{0.8}O_x$	0.0005	×61,000

Table 2-3. Mass normalized initial reaction rates summarized from Figure 2-5.

Electrochemically, the overpotential at which IrO_x catalysts produce a current density of 10 mA cm⁻² for water oxidation to $O_2(g)$ is 250 – 400 mV less than that of $Mn_ySb_{1-y}O_x$ catalysts, depending on the exact composition of the material.^{19-20, 64} Given a Tafel slope between 60 – 120 mV/dec for the IrO_x and $Mn_ySb_{1-y}O_x$ catalysts, it is reasonable that the powdered $Mn_ySb_{1-y}O_x$ catalysts evolved oxygen at a rate that is 2–4 orders of magnitude lower than that of IrO_x .^{20, 98-99}

The global annual production of Mn and Sb is 1.6×10^7 and 1.3×10^5 metric tons, respectively.¹⁰⁰ The global annual production of Ir is under 7 metric tons, so the production of Mn and Sb exceeds the production of Ir by a factor of 2.4×10^6 and 1.9×10^4 , respectively.¹⁰¹ Furthermore, Ir is produced indirectly as a byproduct of other precious metals, so it is not clear if production rates can be readily increased to meet rising demand.¹⁰² At current market prices of bulk Ir (\$196,000,000 per tonne),¹⁰³ Mn (\$2,060 per tonne),¹⁰³ and Sb (\$6,100 per tonne),¹⁰⁴ the raw materials prices for the Mn_ySb_{1-y}O_x catalyst components are about $3 \times 10^4 - 1 \times 10^5$ times cheaper than iridium. However, given the early stage of development of this technology, it is not clear that a full-scale system would be favored in either performance or cost relative to current commercial PEM electrolyzers. The potential benefits of eliminating product gas crossover, mitigating separator degradation, and added operational flexibility are notable.^{69, 79-80, 105-106}

2.4 Conclusions

In summary, powders of the $Mn_ySb_{1-y}O_x$ catalyst family were synthesized by grinding Mn and Sb precursor powders together and calcining at high temperature. Ce-mediated decoupledelectrolysis occurred over the catalysts, and the activity towards oxygen evolution increased with higher Mn composition in the same ratio as previous reports of the electrochemical activity of this catalyst family. Analysis by XPS and UV-visible spectroscopy indicated that the Mn³⁺ state is more prevalent in Mn_y -rich catalysts, correlating with a higher activity towards oxygen evolution, in agreement with previous studies. Shifting the potential of the Ce^{4+/3+} redox couple by changing the acid allowed determination of a chemical Tafel slope of ~100 mV/dec. The catalyst stability, as indicated by the TON and ICPMS, increased as more Sb was introduced into the catalyst, up to a composition of approximately Mn_2SbO_x . This catalyst family thus exhibits promising performance as a chemical water oxidation catalyst, especially when compared to the scarcity and expense of Ir-based catalysts and may prove to be a useful step in the development of earthabundant catalyst inks for PEM electrolyzers.

2.5 Supplemental Calculations and Discussion



2.5.1 Electrical Conductivity Measurements

Figure 2-15. Electrical conductivity measurements collected from hot-pressed catalyst pellets and measured with a four-point probe

Measurements performed using the 4-point probe method were converted to electrical conductivities using standard relations.¹⁰⁷ The dimensions of the hot-pressed catalyst pellets were measured with calipers, and are listed in Table 2-4 below.

Powder Composition (Mn _y)	t (mm)	d (mm)	Conductivity $(S/m \times 10^6)$
0.8	0.47	6.1	2.65
0.6	0.66	6	1.12
0.4	0.6	6.1	0.05
0.2	1.21	6	0.01

Table 2-4. Physical Dimensions and computed conductivity for Mn_vSb_{1-v}O_x powders.

The conductivity decreased by a factor of nearly 25 between the $Mn_{0.6}$ and $Mn_{0.4}$ catalysts, whereas the reaction rate decreased by only a factor of 4 (from 0.08 to 0.02 mL/ mg h) between these two catalysts. The electrical conductivity of the particles is thus not the primary driver of the observed change in reaction rate. However, if this catalyst material were added to an electrode support for utilization in electrochemical oxygen evolution, the electrical conductivity of the powder catalysts could play a more important role in increasing the resistive overpotential of the catalyst layer.

2.5.2 Note on XP Fitting

Regarding the fit for the Mn 2p spectra, Mn^{2+} , Mn^{3+} , and Mn^{4+} peaks were fit to each of the catalyst samples. However, the $Mn_{0.4}$ sample was the only sample that had enough high binding energy signal to require a substantial amount of Mn^{4+} to be present in the fit. The green peaks representing Mn^{4+} in the $Mn_{0.4}$ Mn2p peaks in Figure 2-2 constitute only 16% of the total peak area. The fit for the $Mn_{0.4}$ sample was re-fit without the Mn^{4+} peaks and is shown below for comparison (Figure 2-16). The peak-fitting package is missing a higher binding energy component between ~642-645 eV, which is resulting in a poor fit in this range. This is where the Mn^{4+} peaks are located in Figure 2-2.



Figure 2-16. XP spectra of the Mn 2p orbital of the $Mn_{0.4}Sb_{0.6}O_x$ catalyst, refit without the Mn^{4+} peak package. In order to confirm the oxidation state as estimated by the peak fitting model of the Mn 2p spectra, the peak position of the Mn 3p spectra has been included as well (Figure 2-17). The

position of this peak is shown in relation to literature values of the 3p peak position of pure Mn oxides.^{81-85, 87-88} Shaded areas indicate a standard error between the literature sources.



Figure 2-17. Peak binding energy position of Mn 3p XP spectra compared to literature values for pure Mn²⁺, Mn³⁺, and Mn⁴⁺ oxides, with standard error from between sources shown as shaded regions.^{81-85, 87-88}

The estimated oxidation state from Mn 3p XP spectra is in line with the Mn 2p spectra, in that at high Mn_y, the primary oxidation state of Mn within the $Mn_ySb_{1-y}O_x$ catalyst is Mn^{3+} , and this oxidation state decreases towards Mn^{2+} as Mn_y decreases.

2.5.3 Calculations of Reaction Rate Order

The first-order kinetic fit of the chemical OER data shown in Figure 2 was obtained by fitting a line to a plot of $\ln([Ce^{4+}])$ vs. time. One such linearization, as well as the fitted slopes and intercepts, is shown for the Mn_{0.8}Sb_{0.2}O_x catalysts in Figure 2-18.



Figure 2-18. First order kinetic fit of Mn_{0.8}Sb_{0.2}O_x catalysts.

The resulting fits are shown in Figure 2-19 for the same catalysts as black lines overlaid on the data points. The dotted lines are tangent lines at t = 0 and represent the initial reaction rate. The fit shown in Figure 2-4 is the average and standard deviation of the black lines in Figure 2-19.



Figure 2-19. O_2 generation vs. time data for the $Mn_{0.8}Sb_{0.2}O_x$ catalysts, with individual 1st order kinetic fits shown.

The same process was performed for the rest of the range of Mn_ySb_{1-y}O_x catalysts.

Chapter 3:

Spontaneous Mesostructure Formation Produces Optically Transmissive Ni-P Films That are Catalytically Active for the Photoelectrochemical Hydrogen Evolution Reaction

3.1 Introduction

Photoelectrochemical (PEC) water splitting often requires coating semiconducting light absorbers with metal or metal-oxide electrocatalysts to drive the hydrogen- and oxygen-evolution reactions, respectively.¹⁰⁸ Typically, the integration of catalysts with light absorbers entails optimization of an inherent trade-off between catalytic activity and optical transmissivity. Increasing the mass-loading of the catalyst generally increases the catalytic activity of the photoelectrode per unit of projected electrode area, but blocks additional light from reaching the semiconductor substrate under front-face illumination.¹⁰⁹

Approaches to control the macro- and micro-structure of catalysts to obtain increased optical transmissivity include lithographic, 3D electrode fabrication, and device design processes. Lithographic techniques and control over the thickness of the catalyst layer have been utilized to coat films of catalytic materials on semiconductor surfaces.³⁶⁻³⁷ Microstructuring of semiconductor substrates into microwires, cones, or other morphologies, followed by selective placement of electrocatalysts, has been utilized to obtain high loadings of Ni-Mo, Co-P, Pt, Cu, and others materials for PEC electrolysis or CO₂ reduction reactions, producing increases in energy-conversion efficiency when compared to planar electrode counterparts.^{35, 38-42} Controlled electrodeposition techniques have been used to pattern catalysts in discrete islands, allowing for light to pass between the particles.¹¹⁰⁻¹¹¹ Additionally, several template-free microstructuring approaches have been used to produce desirable microscale patterns over large areas.¹¹²

Electrodeposited Co-P films that initially are dense, metallic, and optically opaque develop cracks upon exposure to acidic environments, allowing for a substantial amount of incident illumination to reach the semiconductor substrate.¹¹³ This structuring occurs spontaneously and does not require external patterning or structure-directing agents. We report herein the implementation of this approach for another electrocatalytic film, Ni-P, that also allows use of earth-abundant elements, as opposed to platinum group metals, to catalyze the hydrogen-evolution reaction while allowing for high optical transmission to an underlying photocathode for use in PEC-based solar fuel production.

3.2 Materials and Methods

3.2.1 Materials:

Copper sheets (Cu, 99.999%, Alfa Aesar), indium-gallium eutectic (In-Ga, 99.99%, Alfa Aesar), sodium hypophosphite monohydrate (NaPO₂H₂·H₂O, Sigma), nickel chloride (NiCl₂, 98%, Sigma), boric acid (H₃BO₃, >99.5%, Sigma), and sodium chloride (NaCl, 99%, Macron Chemicals) were commercially available and used as received. Sulfuric acid (H₂SO₄, TraceMetal grade, Thermo Fisher Scientific), and hypophosphorous acid (H₃PO₂, 50% weight in water, VWR International) were diluted with deionized water with a resistivity of >18.2 MΩ·cm produced by a Barnstead Nanopure system. 100 mm diameter, 525 µm thick n⁺-type (100)-oriented Si wafers with a nominal resistivity of < 0.005 Ω·cm, and p-type (100)-oriented Si wafers of the same dimensions with a nominal resistivity of 1-10 Ω·cm, were purchased from Addison Engineering.

3.2.2 Working Electrode Fabrication:

15-30 mm² chips of n⁺-Si or doped homojunction n⁺-p-Si were used as the substrates for working electrodes. To promote adhesion between the substrates and the electrochemically deposited layer, metallic Ti and then Ni were each sputtered (AJA Orion) onto the samples for 90 s at deposition powers of 130 W and 100 W, respectively, Ohmic contacts were formed by scratching In-Ga eutectic into the backside of the chips with a scribe. Insulated Sn-coated Cu wires with stripped ends were fed through a 6 mm borosilicate glass tube. The wire was sealed into the glass tube using epoxy (Hysol 9460). Samples were attached to the wire with Ag paint that had a grain size < 1.0 μ m (PELCO, Ted Pella), and the back of the electrode was sealed using clear nail polish (Sally Hansen). After the film had been deposited, the sealant was readily removed with a razor blade and the sample was separated from the wire. To prepare electrodes with Cu substrates, a Cu sheet was hand polished using a circular motion for 5 min for each different grit size: 2400 (European FEPA standard), followed by 3000, and then by 4000. This sheet was cut with scissors into smaller 10-20 mm² pieces. The Cu substrates were attached to an electrode assembly by the same process as described above for Si substrates, but without the In-Ga contact.

3.2.3 Film Deposition:

Shortly before film deposition, metalized n⁺-Si samples were sprayed with deionized H₂O and dried under a stream of N₂(g). The Cu substrates were etched for 60 s in 6.6 M HCl(aq) to remove surface oxides. Electrodeposition of the NiP film was performed in a single-compartment borosilicate glass cell that contained 0.15 M H₃BO₃, 0.10 M NaCl, 0.30 M H₂NaPO₂ \cdot H₂O, and 0.20 M NiCl₂. The pH of the solution was adjusted from 6.5 to 3.5 by dropwise addition of H₃PO₂(aq) (10% wt). Control over either the current or potential of the working electrode was

obtained using a Biologic SP-200 potentiostat. The electrolyte was purged with $N_2(g)$ for at least 30 min prior to the deposition and the flow of $N_2(g)$ was maintained during the deposition process. A saturated calomel electrode (SCE) was used as the reference electrode, and a Ni foil electrode was used as the counter electrode.

A thermocouple was immersed directly into the electrolyte to monitor the deposition temperature. The cell was secured to a ring stand with a clamp and held in a water bath so that the water completely surrounded the solution without contaminating the cell. A hot plate was used to raise the temperature of the water bath above room temperature (20 °C). A magnetic stir bar was placed inside the cell and stirring at a rate of 280 RPM was performed for the duration of the deposition. Depositions onto n⁺-Si and Cu were performed at a current density of -20 mA cm⁻². Electrodepositions onto the photoactive n⁺-p-Si/Ti/Ni electrodes were performed using a lightemitting diode (LED) source that had an intensity-weighted average wavelength of 630 nm. In these photoelectrochemical depositions, the working electrode was held potentiostatically at -0.6 V vs. SCE.

3.2.4 Electrochemical Measurements and Physical Characterization

The catalytic behavior of the Ni-P films for the hydrogen-evolution reaction was measured at ambient temperature in 0.50 M H₂SO₄(aq) that was purged with H₂(g). A saturated calomel electrode (SCE) was used as the reference electrode, and a graphite rod was used as the counter electrode. Measurements were obtained using a Biologic SP-200 potentiostat. Photoelectrochemical hydrogen evolution experiments were performed in H₂-purged 0.50 M H₂SO₄(aq) under the equivalent of 100 mW cm⁻² of solar Air Mass 1.5 illumination produced by a calibrated Xe lamp. Energy-dispersive X-ray spectroscopy was used to determine the bulk composition of the NiP films. Measurements were obtained with an FEI Nova NanoSEM 450 with an accelerating voltage of 10 kV. All other observed elements were either attributable to the electrode base (Ti, Si, or Cu) or were negligible in intensity. Scanning-electron microscope (SEM) images were recorded with the same instrument.

X-ray photoelectron spectroscopy (XPS) was performed using a Surface Science M-Probe ESCA/XPS. The chamber base pressure was $< 2 \times 10^{-8}$. The x-ray source was a monochromatic Al K α source. The data were analyzed using CasaXPS computer software. A Shirley background was used for all spectra, which were referenced to adventitious C at a binding energy of 284.8 eV.

Atomic force microscopy was performed using a Bruker Dimension Icon to image the surface morphology of the deposited films. The instrument was operated in ScanAsyst mode using a silicon nitride probe (ScanAsyst-Air). The data were collected using scan areas of 500 nm x 500 nm with a probe velocity 500 nm s⁻¹ and a pixel size of 1.95 nm x 1.95 nm. Raw data were corrected for sample tilt using the Bruker NanoScope Analysis software.

Samples of NiP films electrodeposited onto FTO/Ti/Ni substrates were analyzed using a Cary 5000 UV-vis-NIR with an integrating sphere. Optical transmission measurements were performed after subsequent etching cycles of the same samples at open circuit in 0.50 M $H_2SO_4(aq)$.

Samples of NiP films electrodeposited onto n⁺Si/Ti/Ni substrates were removed from the electrode body by use of a razor blade. The nail polish used to seal the back-contact of the electrode was rigorously removed with the razor blade and isopropyl alcohol, when necessary. The sample chips were then placed in screw cap septum vials (2 mL) and submerged in a mineral oil bath. The bath was stepped from ambient temperature to 200 °C in 25 °C increments. The data shown in

Figure 3 were collected after samples had been held for 10 min at 200 °C. For each measurement, 0.2 mL of the headspace was injected into an Agilent 7890A gas chromatography system equipped with a thermal conductivity detector (TCD), Ar as the carrier gas, a backflush system with a PoraPLOT Q column as the pre-column, and a HP-PLOT Molesieve column as the main column. The quantity of the hydrogen was calculated based on a calibration curve.

The optical properties of the NiP samples were characterized using a spectroscopic ellipsometer with a rotating analyzer (J.A. Woolam Co., Inc.). Data were recorded from 300 to 1100 nm in 10 nm increments at an angle of incidence of 70°. The refractive index (n) and extinction coefficient (k) of the film were determined using a Maxwell-Garnett effective medium approximation.

3.3 Results and Discussion

3.3.1 Material Characterization and Electrodeposition Behavior

Ni-P films were grown by cathodic electrodeposition on Si electrodes that had been preseeded with ~2 nm of sputtered Ni on top of a thin sputtered layer of Ti. The deposition bath was an aqueous solution of 0.15 M H₃BO₃, 0.10 M NaCl, 0.30 M H₂NaPO₂·H₂O, and 0.20 M NiCl₂, with the pH adjusted to 3.5 using H₃PO₂. The temperature of the deposition bath was varied between 20 °C and 80 °C.


Figure 3-1. Color optical micrographs of electrodeposited Ni-P films at (a) 20 °C, (b) 20 °C, followed by a 60 s etch in 0.50 M H₂SO₄, (c) 80 °C, (d) 80 °C, after a 60 s etch in 0.50 M H₂SO₄. Grey areas are the Si substrate. Atomic force micrographs of electrodeposited Ni-P films at (e) 20 °C, (f) 20 °C followed by a 300 s etch in 0.50 M H₂SO₄, (g) 80 °C, (h) 80 °C followed by a 300 s etch in 0.5 M H₂SO₄.

Color optical micrographs and scanning electron micrographs (SEMs) of Ni-P films that were electrodeposited at a current density of -20 mA cm⁻² for 20 s onto n⁺-Si/Ti/Ni electrodes at 20 °C (NiP_{20°C}) showed smooth, reflective layers of Ni-P that were ~ 90 nm thick (Figure 3-1a,Figure 3-2, Figure 3-3). During electrodeposition at 20 °C, bubbles formed on the electrode surface, indicative of H₂(g) evolution in addition to deposition of Ni-P (Figure 3-5). Bubbles formed on the NiP_{20°C} surface during subsequent immersion in 0.50 M H₂SO, and after immersion in 0.50 M H₂SO₄, the NiP_{20°C} films appeared darker visually (Figure 3-1b). In contrast, Ni-P films that were electrodeposited at 80 °C (NiP_{80°C}) were lighter in color than as-deposited NiP_{20°C} films and were ~100 nm thick (Figure 3-1c, Figure 3-4). No bubbles were observed visually during electrodeposition at 80 °C (Figure 3-5), indicating that the faradaic efficiency for Ni-P deposition increased as the temperature increased. Anodic stripping of the Ni-P films in a 1 mM H₂SO₄ solution indicated that the faradaic efficiency of Ni-P deposition was ~ 65% for NiP_{20°C} and 95% for NiP_{80°C} (Figure 3-6). This behavior is consistent with previous observations that the faradaic efficiency of Ni-P deposition increases as the temperature of the deposition bath increases.¹¹⁴⁻¹¹⁵ The voltage required to maintain the deposition current density at -20 mA cm⁻² was more positive (-0.65 V vs. the saturated calomel electrode, SCE) at 80 °C than at 20 °C (-0.92 V vs. SCE), consistent with the electrodeposition behavior of other nickel alloys.¹¹⁶ NiP_{80°C} films did not show a substantial color change as a result of immersion in 0.50 M H₂SO₄ (Figure 3-1d). Atomic force micrographs (AFMs) showed that immersion in 0.50 M H₂SO₄ resulted in cracks through the NiP_{20°C} films (Figure 3-1e-f), whereas NiP_{80°C} films showed no change in morphology due to immersion in 0.50 M H₂SO₄ (Figure 3-1g-h).



Figure 3-2. Cross-sectional SEMs of as-deposited Ni-P films with a cathodic charge density passed of 400 mC cm⁻² in electrodeposition baths at (a) 20 °C, (b) 40 °C, (c) 60 °C, and (d) 80 °C.



Figure 3-3. Cross-sectional SEMs of as-deposited Ni-P films at 20 °C, for a range of cathodic charge density passed between 100-400 mC cm⁻².



Figure 3-4. Thickness of deposited films as determined from cross-sectional SEMs in (a) Figure S1 for films deposited at 400 mC cm⁻² (b) from Figure S2 of films deposited at 20 °C over a range of cathodic charge density, and (c) of films deposited at 80 °C over a range of cathodic charge density.

Cross-sectional SEMs used to determine the thickness of electrodeposited films were based on *n* > 7 measurements from multiple spots along duplicate samples. The Ni-P film thickness was determined to be ~90-100 nm at all temperatures, when 400 mC cm⁻² of charge density was passed during electrodeposition (Figure 3-4a). The measured film thicknesses deposited at 20 °C and 80 °C increased linearly as a function of the charge density passed (Figure 3-4b-c). A linear fit showed the growth rates to be 0.23 nm cm² mC⁻¹ and 0.26 nm cm² mC⁻¹ for the NiP_{20°C} and NiP_{80°C} films, respectively. Forcing the line in S3c through the origin reduces the rate to 0.24 nm cm² mC⁻¹, and a straight line fit through the origin to the point at 400 mC cm⁻² changes the rate to 0.255 nm cm² mC⁻¹. Measurements for the NiP_{20°C} films were taken across the top of the film, so the reported deposition rate is likely an overestimation as those films were not as conformal in cross-section as films deposited at higher temperatures.



Figure 3-5. Still frames taken from videos of electrodeposition of Ni-P at -20 mA cm⁻² onto n⁺Si/Ti/Ni electrodes in Ni-P deposition baths at A) 20 °C and B) 80 °C.

Figure 3-5a shows the presence of $H_2(g)$ bubbles across the entire surface of the n⁺Si/Ti/Ni working electrode while the electrode was passing -20 mA cm⁻² in a deposition bath at 20 °C. Figure S4b shows the surface of an identical electrode at -20 mA cm⁻² in a deposition bath at 80 °C. The slight yellow hue in Figure S4b is due to the yellow/beige-colored top surface of the hot plate that was used to heat the deposition solution.



Figure 3-6. (a) Summary of anodic stripping measurements demonstrating the faradaic efficiency of Ni-P electrodepositions at 20°C (blue) and 80°C (red), as well as dashed lines showing expected values at 65% and 95% faradaic efficiency, (b) net anodic charge density passed under a linear sweep of potential for films deposited at 20°C, (c) net anodic charge density passed under a linear sweep of potential for films deposited at 80°C.

The change in the nanoscale morphology of NiP_{20°C} films due to immersion in H₂SO₄ increased the amount of incident illumination that reached the semiconductor substrate. The resulting increased light absorption by the substrate resulted in the visual darkening of the overlying NiP_{20°C} films. In contrast, NiP_{80°C} films did not undergo substantial morphology changes, or display visual changes, due to immersion in 0.50 M H₂SO₄.

Energy-dispersive X-ray spectroscopy (EDX) indicated that the Ni-P films were Ni-rich, with an initial atomic Ni fraction of 92% and 89% for NiP_{20°C} and NiP_{80°C} films, respectively (Figure 3-7). X-ray photoelectron spectroscopy (XPS) of the P 2p and Ni 2p regions indicated the formation of Ni-P bonds and showed a decrease in surface Ni-O and P-O formation as the deposition temperature increased (Figure 3-8, Table S1). The formation of surface oxides is consistent with a more highly reactive, and therefore more unstable Ni-P surface as the deposition temperature decreased. After immersion for 300 s in 0.50 M H₂SO₄, EDX indicated a decrease of the composition in the bulk of NiP_{20°C} films to an atomic Ni fraction of 88%, whereas no significant change was observed in the composition of NiP_{80°C} films. This behavior is consistent with previous reports of preferential dissolution of Co from Co-P during exposure to acidic electrolytes.³⁹



Figure 3-7. Nickel composition of deposited Ni-P films before (light blue circle) and after (dark blue circle) etching for 300 s in 0.50 M H₂SO₄(aq) as determined by EDX from \geq 12 regions of replicate samples.



B)



P 2p

A)

Figure 3-8. XP spectra of the A) P 2p and B) Ni 2p orbitals of the range of Ni-P films. Dashed vertical lines in A) indicate literature values for the position of the 2p doublet for elemental P.

The peaks in Figure 3-8 were fit utilizing a Shirley background, with the C 1s peak calibrated to 284.8 eV. The P 2p peaks in Figure 3-8a were fit as doublets with a separation of 0.86 eV, a relative peak area ratio $2p_{3/2}$: $2p_{1/2}$ of 2:1, and the same FWHM within a doublet. The position of the P $2p_{3/2}$ peak was 129.1 eV, 129.3 eV, 129.4 eV, and 129.4 eV for NiP_{20°C}, NiP_{40°C}, NiP_{60°C}, and NiP_{80°C}, respectively. The literature value for the P $2p_{3/2}$ peak of elemental P is 130.2 eV,

meaning that the peak position of P $2p_{3/2}$ in the Ni-P films was shifted by ~ 1 eV. Such a substantial shift in peak position is indicative of a partial negative charge on the P species, which is consistent with the formation of Ni-P bonds. The peak area ratio of the P^{δ -} (Ni-P) to P-O signals is shown in Table 3-1. The Ni 2p spectra showed a prominent peak at ~852.5 eV, which is consistent with both the presence of metallic Ni and Ni-P. The complete deconvolution of the Ni 2p spectra, as is the case with any transition metal, is complicated by the amount of Ni multiplet-splitting, a range of stable oxidation states, the presence of multiple nickel oxides, and the presence of shake-up peaks. Additionally, the Ni signal will not be affected by the introduction of P as substantially as the P signal is affected by the Ni, due the low fraction of P in these Ni-P films. However, the decrease of the Ni-O peak relative to the Ni/Ni-P peak is readily quantifiable and is also shown in Table 3-1.

Deposition Temperature (°C)	$P^{\delta-}$: P-O	Ni+NiP : Ni-O
20	0.9	1.2
40	1.2	1.2
60	1.9	1.5
80	1.9	1.6

Table 3-1. Areal Ratio of Ni and P Signals to Surface Oxide Signals.

For both the P 2p and Ni 2p spectra, the presence of P or Ni oxides, respectively, decreased as the deposition temperature increased. This monotonic decrease in the presence of surface oxides is directly evident by comparing the size of the oxide peaks in Figure 3-8a and b to the P^{δ} and Ni/Ni-P peaks, respectively. As is the case with other surface oxides, these oxides may have formed after the electrodeposition step, when the electrodes were exposed to atmospheric ambient conditions. More reactive surfaces are more susceptible to surface oxidation, so the surface reactivity that results in surface oxidation may be the same instability that results in the eventual cracking of films deposited at low temperatures.

3.3.2 Film Cracking and Transmission Enhancement

Cyclic voltammograms of NiP_{20°C} films on photoactive n⁺p-Si/Ti/Ni substrates showed an increase in the cathodic photocurrent density at 0 V vs. RHE (J_{ph}) due to electrochemical cycling in 0.50 M H₂SO₄ that was purged continuously with H₂(g) (Figure 3-9a, blue). Between voltammograms, samples were held at open circuit (~ 0 V vs the reversible hydrogen electrode, RHE) for 180 s in the absence of illumination. The $|J_{ph}|$ of NiP_{20°C} increased from 5.3 mA cm⁻² to 12.1 mA cm⁻² over the activation period. The onset potential for cathodic current did not shift during the activation period, indicating no loss in catalytic activity. Over the same activation period, $|J_{ph}|$ of NiP_{80°C} only increased from 4.2 to 4.5 mA cm⁻² (Figure 3-9a, red). SEMs of NiP_{20°C} showed crack formation during device operation, with a final void fraction of ~20% (Figure 3-9b), whereas no apparent cracks were observed for NiP_{80°C} (Figure 3-9c). The onset potential of n⁺p-Si/Ti/Ni coated with NiP_{80°C} films was ~150 mV more negative than the onset potential of n⁺p-Si/Ti/Ni coated with NiP_{20°C}.



Figure 3-9. (a) Cyclic voltammograms of Ni-P films on n⁺p-Si/Ti/Ni electrodes in 0.50 M H₂SO₄ purged continuously with H₂(g). (b) Representative SEM of a sample deposited at 20 °C after photoelectrochemical experiments in 0.50 M H₂SO₄. (c) Representative SEM of a sample deposited at 80 °C after photoelectrochemical experiments in 0.50 M H₂SO₄.

The optical transmission (T_{opt}) of Ni-P films deposited onto a fluorine-doped SnO₂ (FTO) substrate increased as the etch time increased (Figure 3-10). The average transmission ($T_{opt,avg}$) for as-deposited FTO/Ti/Ni/NiP_{20°C} was 13% between 400 and 1100 nm. After immersion for 300 s in 0.50 M H₂SO₄, T_{opt,avg} increased to 35%, and the void fraction of the film was ~8% (Figure 3-10-Figure 3-11). Although the optical transmission should increase as the void fraction increases because $k_{\text{voids}} < k_{\text{NiP}}$, a densely packed, unetched Ni-P layer with an equivalent fractional coverage of 92% would transmit much less light than the spontaneously nanostructured NiP_{20°C} films. When the constituent components of a film are small relative to the wavelength of light, light is preferentially passed through the voids in the film due to a screening surface charge.¹¹⁰ After 300 s of immersion in 0.50 M H₂SO₄ at open circuit, T_{opt,avg} increased by 170%, 72%, 29%, and 37% for Ni-P films deposited at 20 °C, 40 °C, 60 °C, and 80 °C, respectively. No cracks deeper than 25 nm formed for NiP_{60°C} or NiP_{80°C} films, so the moderate increase in transmission is consistent instead with the formation of shallow < 20 nm cracks (Figure 3-12). NiP_{80°C} films were less transmissive after immersion for 300 s ($T_{opt,avg 80^{\circ}C, 300s} = 8.6\%$) in 0.50 M H₂SO₄ than the other films were before etching ($T_{opt,avg 20-60^{\circ}C, 0s} = \sim 12\%$).



Figure 3-10. $T_{opt,avg}$ of Ni-P films on FTO substrates compared to the void fraction after immersion in 0.5 M H₂SO₄ for 0 s, 60 s, 180 s, and 300 s determined utilizing a Cary 5000 UV-Vis with an integrating sphere ($T_{opt,avg}$, left) and a FEI Nova NanoSEM 450 (void fraction, right).



Figure 3-11. SEMs of NiP films (A-D) as-deposited from 20° C to 80° C; (E-H) after etching for 300 s in 1.0 M H₂SO₄(aq); and (I-L) the same images as (E-H), converted to a black-white 8-bit image to approximate the void fraction. Estimates for the void fraction are shown in red.



Figure 3-12. AFMs of NiP films (A-D) as-deposited from 20 °C to 80 °C; (E-H) after etching for 300 s in 1.0 M $H_2SO_4(aq)$.

3.3.3 Evidence for and treatment of Hydrogen Embrittlement

Spectroscopic ellipsometry on as-deposited NiP_{20°C} films indicated that the extinction coefficient (*k*) was nearly constant at ~1.5, with a slight overall downward concavity vs wavelength (Figure 3-13a). Upon immersion in 0.50 M H₂SO₄, *k* decreased, which is consistent with an increase in optical transmission. In contrast, as-deposited NiP_{80°C} exhibited a straight sloping increase in *k* from 2 to 4.3 as the wavelength increased. Moreover, the *k* of NiP_{80°C} samples did not change substantially after exposure to 0.50 M H₂SO₄ and *k* of the NiP_{80°C} film resembled that of a pure sputtered Ni film both before and after etching (Figure 3-13a). Upon heating an as-deposited NiP_{20°C} film in air for 1 h at 250 °C h, *k* shifted from ~ 1.5 to yield a straight sloping increase from 1.5 to 3.3 as the wavelength increased. Furthermore, *k* did not change substantially upon exposure of the heated NiP_{20°C} film to 0.50 M H₂SO₄ (Figure 3-13b). Both the shape of *k* and the similarity of *k* before and after exposure to 0.50 M H₂SO₄ indicate that the as-deposited NiP_{20°C} film was converted by thermal treatment to a film that was optically similar to, and as chemically robust as, as-deposited NiP_{80°C}.

Gas chromatographs of the headspace of sealed vials that contained NiP_{20°C}, NiP_{80°C}, and bare Ni samples, respectively, showed that upon heating to 200 °C, NiP_{20°C} samples released a substantially larger amount of H₂(g) than NiP_{80°C} samples, in a ratio of nearly 3:1 above the background (Figure 3-13c). The molar ratio of detected H to Ni in the films (H/Ni) was 0.09 and 0.02 for NiP_{20°C} and NiP_{80°C} films, respectively. Linear sweep voltammograms (LSVs) of asdeposited NiP_{20°C} and NiP_{80°C} films showed a substantial difference in the magnitude and position of the peak anodic current density in an unstirred solution of 1 mM H₂SO₄, 0.85 M MgSO₄, and 0.15 M MgCl₂ purged continuously with N₂(g) (Figure 3-13d). The NiP_{20°C} film showed a peak current density of ~1.2 mA cm⁻² at a potential of -0.26 V vs SCE, as well as a shoulder at more positive potentials. The NiP_{80°C} film only showed a single feature of 0.5 mA cm⁻² at -0.1 V vs. SCE. Previous studies of electrodeposited Ni films have shown that an anodic peak at ~ -0.2 V vs. SCE is indicative of a hydrogen-rich β -Ni phase, whereas an anodic peak at -0.1 V vs. SCE is indicative of a hydrogen-deficient α -Ni phase.¹¹⁷⁻¹¹⁸



Figure 3-13. Extinction coefficient (k) of Ni-P films on Si substrates measured by spectroscopic ellipsometry for as deposited (black) and etched (red) samples of (a) $NiP_{20^{\circ}C}$ (b) $NiP_{80^{\circ}C}$ and sputtered Ni, (c) $NiP_{20^{\circ}C}$ heated to 250 °C in air. (d) Headspace H₂ concentration of $NiP_{20^{\circ}C}$ (blue), $NiP_{80^{\circ}C}$ (red), and bare n⁺Si/Ti/Ni substrate (gray) samples after heating to 200 °C in a sealed vial.

Taken together, the ellipsometry, thermal desorption, LSV, and faradaic efficiency data provide evidence that a major difference between NiP_{20°C} and NiP_{80°C} films is the presence of excess hydrogen in the electrodeposited NiP_{20°C} films. Due to the higher co-generation of $H_2(g)$ during NiP_{20°C} electrodeposition, H₂ can be entrained in the electrodepositing film, creating stresses, causing hydrogen embrittlement, and/or enabling the development of defective areas. Stress corrosion cracking can occur at these defective sites upon exposure of a NiP_{20°C} sample to acidic environments. Consistently, bubbles were released from the surface of the etching $NiP_{20^{\circ}C}$ material, and deep cracks subsequently formed. At 80 °C, the faradaic efficiency for Ni-P deposition is higher than at 20 °C, thus less parasitic hydrogen is formed during deposition, no bubbles were visually present on the electrode surface during electrodeposition, and less hydrogen was entrained in the NiP_{80°C}. Although some surface-level cracking was observed in etched NiP_{80°C} films, trans-film voids did not form on NiP_{80°C} samples, and the NiP_{80°C} samples thus do not become substantially more optically transmissive upon etching. The heated NiP_{20°C} film exhibited similar optical properties to that of an as-deposited NiP_{80°C} film because annealing resulted in a H₂-deficient structure similar to that obtained by depositing the film at 80 °C. In industrial plating applications, thermal treatments are well-known to drive off hydrogen and remove film weakness imparted by hydrogen embrittlement.¹¹⁹⁻¹²⁰

3.3.4 Electrochemical Activity

Cyclic voltammograms of n⁺Si/Ti/Ni/NiP electrodes in 0.50 M H₂SO₄ showed that the overpotential ($\eta_{-10 \text{ mA cm}}$ -2) for the HER, defined herein as the excess potential beyond the thermodynamic minimum value required to produce -10 mA cm⁻² of current density, increased monotonically from -200 mV to -230 mV, -290 mV, and -330 mV vs. RHE for the NiP_{20°C}, NiP_{40°C},

NiP_{60°C}, and NiP_{80°C} films, respectively (Figure 3-14a). The η required for Cu/Ti/Ni/NiP electrodes to produce -10 mA cm⁻² in 0.50 M H₂SO₄ increased over time, with final measured $\eta_{-10 \text{ mA cm}}$ -2 of -250 mV, -300 mV, -380 mV, and -490 mV vs. RHE for the NiP_{20°C}, NiP_{40°C}, NiP_{60°C}, and NiP_{80°C} films, respectively, after 150 min of sustained cathodic current (Figure 3-14b). Figure 3-14c shows the changes in *k* for as-deposited NiP_{20°C} to NiP_{80°C} films as the deposition temperature increased.



Figure 3-14. (a) Cyclic voltammograms of Ni-P films electrodeposited at 20 °C (light blue), 40 °C (dark blue), 60 °C (orange), and 80 °C (red) in 0.5 M H₂SO₄. (b) Overpotential measurements at -10 mA cm⁻² for electrodeposited Ni-P films in 0.5 M H₂SO₄. (c) Extinction coefficient (k) from spectroscopic ellipsometry of electrodeposited Ni-P films on silicon substrates.

The smooth transition in catalytic and optical properties of the Ni-P films deposited between 20 °C to 80 °C indicates that the optical, corrosion-resistance, and catalytic properties of electrodeposited Ni-P films can be directly manipulated by control of the deposition bath temperature. Hydrogen dissolution, adsorption, and/or absorption lowers the overpotential for the HER for electrodeposited catalysts of Ni-S, Ni-P, Co-P, and Fe-Ni.^{118, 121-122} For Ni-P, electrodeposition at room temperature leads to an increased uptake of hydrogen during deposition, reducing the HER overpotential.¹¹⁸ The activity of this family of catalysts is related to their ability to adsorb hydrogen, consistent with the observed improvement in the HER activity for Ni-P films deposited at room temperature relative to films deposited at higher temperatures.

3.3.5 Conclusions

In summary, catalytically active Ni-P films were electrodeposited at a range of deposition bath temperatures. The lower faradaic efficiency for Ni-P deposition at room temperature led to a higher parasitic HER current density during Ni-P electrodeposition, resulting in visible H₂ bubbles on the working electrode surface that entrained H₂ in the depositing NiP_{20°C} layer. The stresses caused by this process were released upon exposure to acidic environments, causing deep cracks to form in the NiP_{20°C} films, thereby allowing light to pass through to the light-absorbing semiconductor substrate. By increasing the temperature during electrodeposition, the parasitic HER is suppressed, which causes the optical properties of the Ni-P film to be similar to the properties of pure metallic nickel. The transition between these two behaviors occurs gradually as the temperatures is varied, facilitating control over the catalytic activity and optical transmissivity of the resulting films.

Chapter 4:

Protection of Silicon Photocathodes in Alkaline Media with Rare Earth Silicates

4.1 Introduction

The coupling of renewable energy sources with the electrolysis of water could allow for the generation of a clean hydrogen, which can be utilized as a fuel for seasonal energy storage, or as a feedstock for heavy industrial applications. Water splitting can be carried out in a modular fashion, where electricity is generated by photovoltaics (PV) and then used by a separate water electrolyzer (E). This operational scheme, called PV+E, could be realized with current technology, but current estimates place the levelized cost of hydrogen from a PV+E system at 3-7 times more expensive than steam reforming, the main method of thermochemical hydrogen production.³⁰ By combining the light absorption and electrochemical steps into a single unit, a photoelectrochemical device (PEC) can be created. PECs are attractive options for efficient and scalable generation of grid scale energy because, compared to PV+E schemes, PECs have a substantial reduction in the balance-of-system costs, reducing projected hydrogen prices to the same level as hydrogen generated via steam reforming.³⁰⁻³¹ However, compared to PV+E systems, this reduction in costs comes with increased design difficulties and constraints.

PEC devices may have a substantial cost benefit over PV+E systems, and are being studied extensively for this reason.³⁰ A PEC device could reasonably reach the LCH range of \$2-4/kg, compared to \$7-20/kg for PV+E systems and \$2/kg for thermochemical steam reforming.³⁰⁻³¹ The integration of water-splitting into a single device, however, requires a delicate coupling of different materials and functionalities. First, a light absorber must be used to generate the charge carriers

and voltage required to run the electrochemical reactions. As these light absorbers are generally unstable in the electrochemical environments required for unassisted electrolysis, more chemically robust materials can be coated onto light absorbers to increase device longevity.⁴⁸ Next, catalysts for each half-reaction must be utilized to efficiently and selectively generate desired products. Finally, an ion exchange membrane is required to separate products, both for system efficiency and safety.¹²³

One possible design for a PEC device utilizes a tandem cell, membrane embedded microwire array, which has been demonstrated experimentally.¹²⁴⁻¹²⁵ The tandem cell configuration has two light absorbers, where the top light absorber has a larger bandgap and the bottom light absorber has a smaller bandgap. The top cell absorbs high energy light, allowing subbandgap light to pass to the bottom cell where it can be absorbed by the smaller bandgap material. By pairing different light absorbers, a more broad range of the solar spectrum can be efficiently absorbed, increasing the net voltage and photocurrent generated, enabling high solar-to-hydrogen (STH) efficiency.¹²⁶⁻¹²⁷ The pairing of two semiconductors is a balance between a material not absorbing light that is sub-bandgap, but losing energy to thermalization losses from absorbing light that is too far in excess of the bandgap energy, which results in promoting electrons too high above the conduction band edge.^{126, 128} The most efficient pairing when this dual-configuration is illuminated with terrestrial sunlight comes from the pairing a 1.8 eV band gap semiconductor in the top cell with a 1.2 eV band gap semiconductor in the bottom cell, resulting in a maximum 24% STH efficiency.¹²⁶ The low band gap semiconductor is a good fit for silicon, which has a band gap of 1.1 eV and is already manufactured at a large scale. The high band gap semiconductor is a good fit for III-V materials, which utilize a mixture of group three and group five elements.¹²⁶ Compared to silicon, there has been less extensive research into III-V semiconductors, although work has

been conducted in evaluating their use in PEC devices,^{48, 125} as well as the fundamental properties that inform the corrosion resistance of such materials.⁴⁴⁻⁴⁷

Structuring the tandem light absorbers into membrane-embedded microwire arrays is one design for integrated PEC devices, although others alternatives have been proposed and are being explored.¹²⁹⁻¹³⁰ Important to all of these designs is the ability of the semiconductor substrate to absorb light, generate electron-hole pairs, separate these charge carriers through the use of some sort of diode-type junction, and eventually pass those charge carriers into solution. Ideally, the semiconductors, separators, and catalysts are constructed in such a way that H₂ and O₂ are by default generated in separated chambers, although this is not considered a strict requirement in some devices. Embedding microwire light absorbers into a membrane support increases collection efficiency and prevents the generation of an explosive gas mixture. The selectivity of the membrane allows for protons (in acid) or hydroxide (in base) to migrate from one side of the cell to the other, balancing the half reactions. Additionally, the membrane serves as a structural support for the microwires, allowing the device to bend and deform without breaking the brittle light absorbers. This membrane embedded microwire design has been shown experimentally.¹³¹ However, this work was a proof of concept for the mechanical, electrical, and optical properties of the design, and the device was not used for water splitting.

Finally, this design incorporates catalysts for both HER and OER, isolated to their respective sides of the device. These catalysts are necessary for driving the water electrolysis reactions selectively and efficiently. While either a strongly acidic or a strongly alkaline electrolyte will need to be utilized in a PEC device, it is not clear which condition is more favorable for efficiency or stability. Both mediums present performance issues for unprotected devices, and both influence the overpotential and stability of catalysts. Review work has found that the most effective

earth abundant catalysts for OER are stable in alkaline conditions, while many common OER catalysts are outright unstable in acidic conditions, readily corroding or dissolving in this electrochemical environment.^{19, 132} Furthermore, protective oxides with optimal conduction band edges or conductive defect states have been identified for the protection of n-type semiconductors.^{48, 133} For these reasons, a significant amount of photoanode research has found success studying materials in alkaline environments. Silicon, the most commonly studied and lowest-cost semiconductor material, etches uncontrollably in alkaline conditions. In contrast, silicon passivates in acidic environments, forming a silicon oxide that slows the corrosion of the underlying material. For this reason, a majority of photocathode research has been conducted in acidic conditions.

Combining these two points, a relative dearth of research has been conducted on photocathodes in alkaline conditions or photoanodes in acidic conditions. Relative stability approaching 100 days for OER devices in base and for HER devices in acid has been demonstrated, but the counterpart for each is underdeveloped by one or two orders of magnitude, leaving great opportunities for advancement in these areas. For this work, HER device stabilization in alkaline conditions will be the focus.

Protection layers deposited with highly conformal methods, including ALD and magnetron sputtering, even when followed by thermal annealing or other post-deposition treatment methods, still have defects that can lead to eventual device failure. Both extrinsic defects, which form through incidental contamination during the synthesis of a protection layer, and intrinsic defects, which are the result of intrinsic (electro)chemical properties of a material, can lead to the formation of pinholes in a protective film.⁵⁰ The presence of a pinhole in certain geometries can expose the underlying semiconductor substrate to solution, causing the entire protection layer to be bypassed,

shortening the lifetime of a device. For this reason, the mechanisms behind pinhole formation, as well as strategies to mitigate failure at pinholes, are often mentioned in PEC protection literature.^{40,} 42, 48, 134

Silicides have been investigated as top coatings for various stability-related applications, including the use of nickel silicide to protect a silicon photocathode for almost 2 weeks of operation in a pH 13.7 environment, due to their stability over silicon in alkaline conditions, ease of creation, and electrical conductivity^{40, 135-139} Although thick films of silicides have been shown to etch negligibly in the time span of hours, cost effective implementation of PEC devices requires negligible material loss over much longer timescales.¹³⁵ Furthermore, while nickel silicide appears to be kinetically stabilized during operation, it is not predicted to be thermodynamically stable at hydrogen evolution potentials in alkaline media, which may cause issues with the long duration operation required for commercial PEC devices.^{40, 140}

Yttrium silicide has been extensively studied due to its ability to form epitaxial, pinhole free layers on multiple silicon faces, including <111> and <100>.¹⁴¹⁻¹⁴⁹ Like nickel silicide, yttrium silicide is not predicted to be thermodynamically stable at reductive potentials in alkaline environments.¹⁴⁰ Unlike nickel silicide, yttrium silicide can be further oxidized to form a yttrium silicate, which is predicted to be stable in alkaline HER conditions.^{140, 142} A variety of rare earth silicates, including yttrium silicate, have been made by annealing silicide layers in air, reactive oxide sputtering under an argon/oxygen plasma, and through atomic layer deposition.^{142, 150-155} Therefore, due to predicted stability and literature precedent for viable growth methods, a yttrium silicate film could be utilized as a protection layer for silicon photocathodes in alkaline environments.

4.2 Materials and Methods

4.2.1 Chemicals

All chemicals were commercially available and used as-received unless otherwise noted. Potassium hydroxide (pellets, 99.99% trace metals basis, semiconductor grade), potassium ferricyanide (>99.0%, ACS reagent), and potassium ferrocyanide (>98.5%, ACS reagent) were obtained from Sigma Aldrich. Chemicals were diluted with deionized water with a resistivity of >18.2 M Ω ·cm produced by a Barnstead Nanopure system. 100 mm diameter, 525 µm thick n+type (111)-oriented Si wafers with a nominal resistivity of < 0.005 Ω ·cm, and p-type (111)oriented Si wafers of the same dimensions with a nominal resistivity of 1-10 Ω ·cm, were purchased from Addison Engineering.

4.2.2 Sample Preparation and Working Electrode Fabrication

For samples used in dark-electrolysis experiments (without simulated solar illumination), degenerately doped n^+ -Si substrates were used without further alteration. For samples used as photocathodes under simulated solar illumination, p-Si substrates were doped with an n^+ -Si emitter layer in a thermal doping process in a quartz tube furnace held at 850 °C, under 10 lpm N₂ flow, and with PH-900 PDS wafers as the phosphorous source.

Silicon wafers were cut with a graphite scribe into $\sim 2^{\circ} \times 2^{\circ}$ squares. The silicon substrates were thoroughly cleaned utilizing the RCA corporation standard clean 1 and 2 procedures, followed by submersion in HF immediately prior to sputter deposition. A flowchart of the silicate sample preparation is shown in Scheme 4-1. Preliminary sputtering of metallic yttrium-silicon samples occurred under a pure argon atmosphere. Following sputtering, metallic as-deposited samples were further annealed at 900 °C in either air or argon. Initial annealing in air occurred in

a muffle furnace, where the temperature was ramped at 10 °C/min to the setpoint of 900 °C, followed by a hold of 1 hour, following a ramp back down to room temperature. Later, oxidized materials were sputtered directly by reactive sputtering under a gas flow of a 16/4 sccm mix of Ar/O₂, at a deposition pressure of 5 mTorr. Reactive sputtering of silicate samples occurred from Y and p-Si sputtering targets (ACI Alloys, 99.9%) at 180 W and 72 W, respectively, for 3 hours, which deposited approximately 100 nm of the mixed oxides. Sputterer deposition times were adjusted to linearly alter the thickness of deposited material. Following direct deposition of oxidized Y₂SiO₅, high temperature annealing in either air or Ar occurred in a tube furnace that had been pre-heated to 900 °C. As-deposited silicate samples were pushed gradually into the tube furnace over the course of 1 minute, were left at process temperature for 2-5 minutes, then removed slowly over the course of 1 minute.



Scheme 4-1. Sample Preparation Flowchart

Following any post-deposition annealing procedure, silicate-coated silicon samples were fashioned into electrodes for electrochemical testing. 15-30 mm² chips of n⁺-Si or doped homojunction pn⁺-Si were used as the substrates for working electrodes. Ohmic contacts were formed by scratching In-Ga eutectic into the backside of the chips with a scribe. Insulated Sn-coated Cu wires with stripped ends were fed through a 6 mm polyethylene tube. Samples were attached to the wire with Ag paint that had a grain size < 1.0 μ m (PELCO, Ted Pella). The wire and exposed ohmic contact was sealed into the tube using a Gorilla Glue two-part epoxy.

4.2.3 Experimental Details

Corrosion experiments were conducted in 1 M KOH with electrodes held at either open circuit or at a negative potential, as noted. The solution was continuously stirred and purged with H₂(g) during measurements. The reference electrode was a CHI152 Mercury Oxide reference. KOH etches glass (SiO₂), so any inclusion of glass components was avoided in order to avoid excess contamination of silicon into solution over time. An entirely glass-free electrochemical cell was utilized for corrosion experiments. A screw-top polyethylene (PE) jar was used as the cell body, with holes drilled in the lid for electrode access. Electrode bodies were constructed with plastic tubing, while the epoxy used to seal the working electrode face was Gorilla Glue two-part epoxy. These components were tested without the presence of a silicon working electrode and found to corrode negligibly via ICP-MS.

For ICP-MS, 1 mL aliquots of solution were taken periodically over the runtime of the electrode. 0.5 mL of a collected aliquot was diluted to 5-10 mL with either 2% or 5% nitric acid, depending on the specific experiment. ICP-MS standards were made through serial dilution of a

known ICP-MS standard of Si dissolved in 5% nitric acid. Fresh, as-prepared KOH was added to the standards in order to rigorously matrix match the standards to the diluted KOH aliquots.

Activity, stability, and conductivity experiments on degenerately doped substrates occurred in 1 M KOH, which was continually stirred and purged with $H_2(g)$. Experiments on photoactive substrates occurred in the same conditions, with the addition of illumination from the equivalent of 100 mW cm⁻² of solar Air Mass 1.5 illumination produced by a calibrated Xe lamp. Photocathode experiments were conducted in glass cells, not plastic cells. Measurements were obtained using a Biologic SP-200 potentiostat.

4.2.4 Characterization Techniques

Energy-dispersive X-ray spectroscopy was used to determine the bulk composition of the Y₂SiO₅ films. Measurements were obtained with an FEI Nova NanoSEM 450 with an accelerating voltage of 10 kV. All other observed elements were either attributable to the electrode base or were negligible in intensity. Scanning-electron microscope (SEM) images were recorded with the same instrument. SEMs of sample cross sections, combined with profilometry data, were used to determine the thickness of deposited samples.

X-ray photoelectron spectroscopy (XPS) was performed using a Surface Science M-Probe ESCA/XPS. The chamber base pressure was $< 2 \times 10^{-8}$. The x-ray source was a monochromatic Al K α source. The data were analyzed using CasaXPS computer software. A Shirley background was used for all spectra, which were referenced to adventitious C at a binding energy of 284.8 eV.

Samples of Y_2SiO_5 films sputtered onto both silicon and quartz substrates were analyzed using a Cary 5000 UV-vis-NIR with an integrating sphere. Silicate samples on silicon substrates were utilized to determine the reflectance. Silicate films were deposited onto quartz samples to determine film transmittance. For transmittance measurements, a bare quartz substrate was used as the baseline for 100% transmission.

4.3 **Results and Discussion**

4.3.1 Characterization of Yttrium Silicate Films

Ytrrium silicate films were reactively sputtered under a mixed argon-oxygen atmosphere to directly deposit oxidized materials, rather than the metallic materials that would result from typical sputtering in an argon atmosphere. XP spectra of as-deposited yttrium silicate films showed that the Y 3d and Si 2p spectra were primarily composed of yttrium silicate, with no apparent contributions from pure yttrium or silicon oxides (Y₂O₃ or SiO₂, respectively) (Figure 4-1). Upon further annealing in either air or Ar, the Y 3p peaks shifted to higher binding energies by ~0.3 eV, indicative of a slightly more oxidized yttrium in the near-surface region.



Figure 4-1. XP spectra of silicate films deposited in a mixed argon-oxygen atmosphere. Films shown are as-deposited (blue), further annealed in air (purple), or further annealed in Ar (green).

Yttrium silicate films sputtered under a mixed argon-oxygen plasma were dark purple to light blue in color when deposited onto silicon substrates, with color depending on the thickness of the film (Scheme 4-1). This range of colors is indicative of an anti-reflective surface, where the colors come from an interference of light reflected from the top surface of the silicate with the light reflected from the top surface of the silicon substrate.¹⁵⁶ UV-Vis spectroscopy of silicate films deposited onto silicon substrates indicated that samples became less reflective as the thickness of the film increased, with a maximum occurring when the film was 90 nm thick (Figure 4-2). Likewise, transmission spectrum of a 90 nm silicate film deposited onto a quartz substrate showed that >90% of the incident illumination was transmitted through the silicate film.



Figure 4-2. Reflectance measurements of yttrium silicate films deposited on silicon substrates (left) and transmission of silicate film deposited on quartz substrate (right).

Antireflective properties are beneficial to the performance of PEC devices, as increasing the amount of light that is transmitted to the semiconductor substrate increases the maximum efficiency of the device. Because antireflection is tuned by adjusting film thickness, this parameter may be arbitrarily optimized for increased performance. The effect on increasing film thickness on the electrical conductivity of the film is discussed in later sections.

4.3.2 Assessing the Corrosion Properties of Yttrium Silicate Films

Yttrium silicate films were initially selected for the application of protection of silicon photocathodes in alkaline environments due to their expected thermodynamic stability in this electrochemical environment. Homojunction pn^+ -Si devices rely on an ~100 nm thick n^+ -type emitter to spatially separate photogenerated charge carriers to avoid losses due to recombination. Although the entire silicon photocathode is ~350 µm thick, the loss of just the 100 nm emitter layer is sufficient to deactivate the entire device. Therefore, achieving high enough resolution to monitor the top 100 nm of a device is necessary to study the overall stability of silicon homojunction photocathodes. For this reason inductively coupled plasma mass spectrometry (ICP-MS), which is capable of detecting dissolved species in the ppt range, was utilized to detect silicon etching from the silicon substrate.

When held in 1 M KOH at open circuit, ICP-MS measurements indicated that even 2 nm of as-deposited, non-annealed, sputtered yttrium silicate substantially reduced the rate of silicon corrosion from ~1,300 nm/hr to 54 nm/hr (Figure 4-3). Increasing the thickness of the yttrium silicate layer to 30 nm or 90 nm further decreased the rate of silicon corrosion to ~6.5 nm/hr, with no substantial difference between the corrosion rate of silicon protected by 30 nm or 90 nm silicate films.



Figure 4-3. Corrosion of silicon protected by non-annealed (as deposited) yttrium silicate films at open circuit in 1 M KOH.

Annealing as-deposited silicate protection layers in either air or argon at 900 °C further decreased the etch rate of silicon at open circuit in 1 M KOH (Figure 4-4, Figure 4-5). After annealing in air, a 2 nm silicate reduced the corrosion rate of Si to 9 nm/hr, while increasing the thickness to 30 nm further decreased the corrosion rate to 0.4 nm/hr. Films \leq 7nm that were annealed in Ar did not substantially reduce the corrosion rate compared to non-annealed samples. However, silicon electrodes coated with 90 nm silicates annealed in Ar had a corrosion rate of silicon of 1.5 nm/hr. Table 4-1 shows a summary of the silicon corrosion rates measured from silicon electrodes coated with yttrium silicate layers of various thickness and subjected to various post-deposition treatments.



Figure 4-4. Corrosion of silicon electrodes protected by yttrium silicate films after annealing in air at 900 °C, held at open circuit in 1 M KOH.



Figure 4-5. Corrosion of silicon electrodes protected by yttrium silicate films after annealing in argon at 900 °C, held at open circuit in 1 M KOH.

Film Thickness	As-deposited	Air annealed	Ar annealed
(nm)	(nm/hr)	(nm/hr)	(nm/hr)
2	49	9.0	121
7	54	0.6	96
30	6.5	0.4	1.3
90	9.0	-	1.5

Table 4-1. Summary of Si corrosion rates from Figure 4-3, Figure 4-4, and Figure 4-5.

Monitoring the open-circuit potential of a silicon electrode coated with 2 nm of yttrium silicate that had been annealed in Ar at 900 °C showed an initial plateau at ~ 0.5 V vs. RHE for the first 24 hours of exposure to 1 M KOH (Figure 4-6, blue line). After ~24 hours of operation, the potential rapidly decreased to -0.2 V vs. RHE, where it held steady for 3 more days. For comparison, the OCV of a bare silicon electrode is included as well, shown to plateau immediately at -0.22 V vs. RHE (Figure 4-6, purple line). The corrosion of silicon from the 2 nm protected silicon device showed no measurable loss of silicon during the first 24 hours of operation, followed by a linear increase of Si concentration after 24 hours (Figure 4-6, orange triangles).

Although ICP-MS is a useful technique for monitoring the corrosion of silicon from silicate-protected (photo)electrodes, it requires careful preparation of samples, strict testing conditions, and a significant amount of processing time. Therefore, identifying a method to determine failure of protected silicon electrodes during (not after) operation in 1 M KOH would be a useful step in rapidly identifying stabilized devices. Comparing the open-circuit potential measurements with ICP-MS corrosion data show a correlation between the onset of silicon corrosion from a protected Si electrode with the decrease in open circuit from the initial value down to the value of an unprotected silicon electrode. These data indicate that for approximately 24 hours, a 2 nm silicate prevents Si corrosion in 1 M KOH, and the potential is situated above RHE. However, upon failure of the protective layer, the OCV moves to the same potential as a

bare silicon sample, and corrosion begins. Awareness of the open circuit potential of a silicon electrode can provide useful real-time feedback on the corrosion of a sample.



Figure 4-6. Overlay of OCV of a bare silicon electrode (purple, left), a silicon electrode protected with a 2 nm silicated annealed in Ar (blue, left), and the measured corrosion of silicon from the Ar annealed sample (orange triangles, right).

So far, analysis of the corrosion of silicon from yttrium silicate protected electrodes has been conducted under open circuit conditions, where no current is flowing. While this is useful to determine if a silicate layer is capable of physically isolating the silicon substrate from solution, as well as a useful step in determining the chemical corrosion resistance of yttrium silicate by itself, open circuit conditions are not representative of a silicon photocathode under operation as a photocathode generating hydrogen. When protected silicon electrodes were held under electrochemical bias at -0.2 V vs. RHE, an electrochemical condition where hydrogen evolution would begin if a proper catalyst were affixed to the electrode surface, corrosion data indicate that silicates maintain their ability to prevent the corrosion of silicon from the underlying silicon substrate (Figure 4-7). Under these electrochemical conditions, a bare silicon electrode corrodes at 232 nm/hr, while an electrode protected by a 30 nm silicate annealed in Ar corroded at 3.5 nm/hr, and an electrode protected by a 90 nm silicate annealed in air corroded at 2 nm/hr.



Figure 4-7. Silicon corrosion from silicon electrodes held at -0.2 V vs RHE in 1 M KOH that are unprotected (blue), protected by an air annealed silicate (orange), and an Ar annealed silicate (purple).

From the observed corrosion of silicon from electrodes protected by sputtered yttrium silicates shown in Figure 4-3 to Figure 4-7, yttrium silicate substantially reduces the corrosion of silicon by multiple orders of magnitude, depending on the post-deposition annealing conditions and on the electrochemical environment. Furthermore, the anti-reflective properties of the silicate films indicate that they are a good candidate for increasing the stability of silicon photoelectrodes without detrimentally stopping illumination from reaching the semiconductor substrate.
4.3.3 Assessing and Increasing the Conductivity of Yttrium Silicate Films

Yttrium silicate is a transparent oxide with a large bandgap of >5 eV.¹⁵⁷⁻¹⁵⁸ Due to poor alignment of the conduction bands of Y₂SiO₅ with silicon, this material forms a barrier to electron conduction from the silicon substrate through the protection layer. As such, the conductivity of electrodes substantially decreases upon being coated with yttrium silicate. Although tunneling through non-conductive layers that are a few nanometers thick is possible, silicate layers ~2 nm thick did not adequately prevent the corrosion of the silicon substrate (Figure 4-3 to Figure 4-5).

Figure 4-8 shows cyclic voltammetry of silicon electrodes in a 0.5 M Fe(CN) $_{6}^{3-}/0.5$ M Fe(CN) $_{6}^{4-}$ redox couple in water. Each electrode was decorated with a sputtered Pt layer, which allows for the facile transfer of electrons to and from the ferri/ferro cyanide redox couple. Compared to an unprotected silicon electrode, which is able to achieve a cathodic current density of -10 mA/cm² at -50 mV vs. Fe(CN) $_{6}^{3-/4-}$, electrodes coated with 30 nm of yttrium silicate which had been annealed in air (green), annealed in Ar (orange), or left as-deposited (purple), achieved the same current density at approximately -600 mV, -500 mV, and -550 mV vs. Fe(CN) $_{6}^{3-/4-}$, respectively. Such a large increase in the electrical resistance of a protection layer on a photoelectrochemical device is too large for efficient operation in solar water splitting. A doped silicon homojunction photocathode generates approximately 550 mV of photovoltage, which would be entirely canceled out due to the additional resistive loses of the yttrium silicate layers. Due to the negative impact of this increased electrical resistance on the efficiency of any solar fuels device, strategies for increasing the conductivity of the yttrium silicate layer, while still maintaining high electrochemical stability, were evaluated.



Figure 4-8. Cyclic voltammetry in a mixture of 0.5 M $\text{Fe}(\text{CN})_6^{3-}/0.5$ M $\text{Fe}(\text{CN})_6^{4-}$ of silicon electrodes coated with yttrium silicate layers annealed in air (green), annealed in Ar (orange), as deposited (purple), all compared to a bare silicon sample with no yttrium silicate protection layer (blue).

Initial methods of increasing the conductivity of yttrium silicate overlayers included cosputtering dopant metals to increase the conductivity through a hopping mechanism,¹³³ and inducing dielectric breakdown of the silicate layer, creating a path that would remain conductive after treatment.¹⁵⁹ Introducing small amounts of platinum to the yttrium silicate film during sputter deposition was not found to enhance the conductivity at the analyzed parameters, although only preliminary work was conducted in this vein.

Solid-state voltammograms taken on a silicon electrode coated with 35 nm of sputtered SiO₂ showed that breakdown of the dielectric material was possible by applying a large voltage to a 3 mm Pt island deposited on top of the material (Figure 4-9). Although initial results showed promise in this method for increasing the conductivity of yttrium silicate layers as well, this method was found to not be consistent between samples or even between breakdown events on the same

sample. Furthermore, the size of the area that needed to be contacted on the top side of the yttriumsilicate layer was too large to be utilized in the standard electrode design, which would have required a significant re-design of experimental methods. Further exploration of this method for increasing the conductivity of insulating layers should be conducted with more specialized equipment to ensure experimental consistency, leading to reproducibility.



Figure 4-9. Solid-state cyclic voltammograms of SiO₂ coated Si electrodes before (blue) and after (red) dielectric breakdown.

Final attempts to increase the conductivity of the yttrium silicate protective coating focused on lithographic techniques to etch holes through the silicate film, followed by filling the holes with sputtered catalytic materials, such as Pt. In doing so, conductive pathways would be made through the protective layer in small areas, while simultaneously maintaining the electrochemical stability of the silicate layer across most of the surface.

An overview of the photolithography, sputtering, and etching process is shown in Scheme 4-2. First, silicate-coated Si samples were coated with photoresist (PR), which was photolithographically patterned with circular holes $10 \,\mu\text{m}$ in diameter, spaced $70 \,\mu\text{m}$ from center to center. These patterned samples were submerged in HF for 30 seconds, causing the exposed silicate circles to be etched away entirely, while a majority of the silicate surface was protected underneath the patterned photoresist. Samples were immediately coated with sputtered Pt, followed by an acetone liftoff of the photoresist. At this stage, the silicon substrates were coated with a largely conformal yttrium silicate later, with the exception of Pt cylinders traversing the film. Gaps between the Pt cylinder and the silicate sidewalls were sources of device failure as KOH was able to penetrate to the silicon substrate, eventually undercutting the protection layer.

For this reason, a second photolithography step aligned a larger $30 \,\mu\text{m}$ hole pattern over the primary pattern. Pt was sputtered onto this pattern, followed by another liftoff step. Incorporating two layers of Pt in this method ensured that no gaps existed between the sidewalls of the platinum and the silicate layer. Finally, additional Pt was electrodeposited onto the substrates to increase electrochemical activity.



Scheme 4-2. Flowchart of photolithography method to increase silicate conductivity through patterning conductive pathways.

SEMs showed successful alignment of the two subsequent photolithography-sputter deposition steps (Figure 4-10). Concentric rings of 10 μ m and 30 μ m Pt can be seen from the first and second photolithography steps, respectively. Side-view SEMs (Figure 4-10b) show a vertical offset between the first and second layer of Pt, likely due to the depth of the hole in the Y₂SiO₅ layer being deeper than the thickness of Pt deposited in the first sputtering step. Deposition of thicker layers of Pt which would entirely fill the 100 nm deep holes etched into the silicate overlayer proved to be too thick for the acetone lift-off step, as the thick Pt layer completely covered the photoresist and did not allow acetone to dissolve the pattern. This mismatch resulted in a seemingly unavoidable offset of thickness in this design, which may have led to poor conductivity and/or served as a failure point for the protected devices.



Figure 4-10. A) SEM of photolithographically patterned yttrium silicate layer, with concentric circles of platinum islands for enhanced electric conductivity and catalytic activity and B) side view SEM photolithographically patterned Pt islands.

A yttrium silicate film deposited onto a pn^+ -Si homojunction substrate, annealed in air for 2 minutes at 900 °C, patterned with Pt catalyst islands as shown in Scheme 4-2, followed by the additional electrodeposition of 800 mC/cm² of Pt, was held in 1 M KOH under simulated 1 sun illumination at 0.0 V vs. RHE and the current density was recorded over time (Figure 4-11).

Extended holds at the thermodynamic onset potential for HER ensures that all current generated is being driven from the photovoltage generated by the homojunction pn^+ -Si substrate, rather than from any external potential applied by the potentiostat. The measured current density at 0.0 V vs. RHE held constant at approximately -23 mA/cm² for 1 day of operation, followed by a decline to -10 mA/cm², where the current held relatively steadily for 3 days.

Cyclic voltammograms showed that the initial photovoltage of the protected device was 500 mV, and that the fill factor was relatively poor at 0.28. Upon operation for 100 hours in 1 M KOH, the J-V curve of the protected photocathode shifted negative by ~250 mV, although the OCV remained relatively stable at 475 mV vs RHE. J-V behavior of an unprotected silicon photocathode, decorated with the same photolithographically patterned Pt catalyst islands and extra Pt electrodeposition as the silicate-protected devices, after 20 hours at 0.0 V vs RHE showed a substantially reduced current density. As the potential applied to the electrode was continually swept to lower potentials, the magnitude of current density increased exponentially, exceeding the initial value of -25 mA/cm², and showed with no indication of plateauing to a light-limited value.



Figure 4-11. A) Current density at 0.0 V vs. RHE for a yttrium silicate protected silicon photocathode in 1 M KOH, and B) cyclic voltammograms of protected silicon photocathode at 0 hours of operation (blue) and 100 hours of operation (red), compared to a bare silicon photocathode with the same Pt catalyst after only 20 hours of operation.

An initial photovoltage of 500 mV is relatively standard for planar, doped pn⁺-Si homojunction devices, indicating that the deposition and annealing of the silicate layer did not substantially alter the underlying junction.^{35, 39} A low fill factor is indicative of a device that requires more substantial overpotentials past OCV to achieve the maximum light-limited current density (in this case about 500 mV), opposed to a device with a high fill factor which could reach the maximum current density at a smaller overpotential (e.g. 100-200 mV). A low fill factor could indicate that the conductive pathways etched through the silicate overlayer were not sufficient to achieve high catalytic activity, or that some other form of electrical or electrochemical resistance is present in the device. After 100 hours of operation, the shifting of the J-V curve ~250 mV negative of the initial curve indicates a further loss of catalytic activity. The slight decrease in OCV (from 500 mV to 475 mV), as well as the plateau of current density at -27 mA/cm^2 indicates that the pn⁺ homojunction is still intact and is still generating the photovoltage required to operate the device, and that the substrate layer has not been bypassed by an electrical shunt. The observed

loss of catalytic activity is instead consistent with losses caused due to fouling of the catalyst overlayer discussed later (see Preparation of Low Impurity KOH section). For comparison, after 20 hours of operation at 0.0 V vs. RHE, the unprotected silicon photocathode appeared to be entirely shunted, with no plateau to a stable photocurrent density. Instead, the current density increases exponentially, in line with a metallic electrode following standard electrochemical kinetics. Compared to the unprotected photocathode, a sputtered yttrium silicate layer enabled a silicon photocathode to achieve relatively stable photovoltage and maximum photocurrent densities over 4 days of operation. However, failure of the catalyst layer led to poor fill factor and ultimately low STH efficiency.

Due to the likelihood of catalyst failure being the cause of overall device failure, the deposition of a higher surface area NiMo catalyst was evaluated as a potential solution. Cyclic voltammograms of yttrium silicate devices decorated with Pt islands as in Figure 4-10, with a further electrodeposition of NiMo at -2500 mC/cm² showed an initial onset and activity similar to devices coated with electrodeposited Pt catalysts from Figure 4-11b, with an open circuit voltage of 500 mV vs. RHE and a light-limited current density of -17 mA/cm² (Figure 4-12). The lower initial photocurrent density of the NiMo decorated devices is likely due to the increased catalyst loading compared to the Pt decorated devices, which blocks more of the incident illumination. Inconsistencies in the smoothness of the initial J-V behavior of the electrode is due to bubbles forming on the surface, which was subsequently fixed by adjusting the solution stir rate.

After 12 days of operation at 0.0 V vs. RHE, the activity of the NiMo catalyst decreased considerably, with the OCV shifting 500 mV negative to 0.0 V vs RHE. The photocurrent density decreased marginally as well to -15 mA/cm². However, unlike the behavior of unprotected photocathodes after merely 20 hours (Figure 4-11b), the NiMo decorated, yttrium silicate protected

photocathodes showed no signs of shunting, indicating that the emitter layer is still present and that silicon etching has not proceeded unchecked.

In order to demonstrate the presence of the emitter layer and verify that loss in performance is due to catalyst fouling/deactivation, an additional -2500 mC/cm² of NiMo was deposited onto the used device. Upon retesting in 1 M KOH, the efficiency of the device once again increased to nearly the initial value. A decrease in the OVC of about 100 mV was noted, which could be due to a slight degradation of the emitter layer, or due to the negative effects of having a lower photocurrent density on the photovoltage of a photoelectrochemical diode.¹⁰⁸ The photocurrent density was lower than the initial value at about 13 mA/cm², which is consistent with a higher loading of catalyst in the second case. Chopping of the incident illumination, as indicated by places where the J-V behavior suddenly jumps to 0 mA/cm² in the red line, indicated that essentially all of the current, even at -1.0 V vs. RHE, is solely photocurrent and that no extensive shunting of the device had occurred.



Figure 4-12. Cyclic voltammograms of yttrium silicate protected silicon photocathodes, decorated with NiMo catalysts.

Taken together, these data indicate that the yttrium silicate overlayer is effective at preventing the corrosion of the n^+ emitter layer of the silicon photocathode, allowing for far longer operation compared to the unprotected counterpart. Utilizing ICP-MS to probe the corrosion of Si from these samples would be useful, however glass cells were used for photocathode experiments due to the favorable transmissivity of light through glass. Construction of an entirely plastic cell with an appropriate viewing window for simulated solar illumination would be an important step in enabling this experiment.

Overall, the photolithographic method of patterning conductive catalyst pathways through an insulating protective layer is sound in theory and could allow for the utilization of essentially any protective overlayer, regardless of electrical conductivity. However, in practice, this method introduces difficulties in sample preparation, introduces sources of device failure, and still fails to completely solve the issue of an insulating overlayer. Even with these restrictions inherent in this method, fixing the issue of catalyst deactivation in these devices would allow for stable chronoamperometry behavior at 0.0 V vs RHE over the course of days or weeks. Multiple researchers in the PEC protection literature have addressed this challenge through a number of electrolyte preparation methods, catalyst regeneration methods, or catalyst re-deposition methods. Although some of these methods were attempted in this work, none were successfully implemented to completely stabilize the catalytic activity of any of the photocathodes.

4.4 Supplemental Calculations and Discussion

4.4.1 Initial synthesis procedure and characterization of yttrium silicate films

Initial deposition of yttrium-silicon films was conducted via magnetron sputtering under an argon plasma. Such deposition conditions resulted in a metallic yttrium-silicide film which was metallic gray in color, as well as optically opaque. Upon annealing metallic silicide films in air, the films were converted to silicate layers, a transparent material which is more highly oxidized than the metallic silicide film.

Figure 4-13 shows the yttrium silicide films as-deposited on quartz under an argon atmosphere, which are metallic and opaque. The transmission of light through these films decreased as a function of film thickness, as indicated by the darkening of the film and diminished ability to see the labwipe behind the quartz substrate. Upon annealing, the films were converted to transparent silicates.



Figure 4-13. Image of as-deposited yttrium silicide films on quartz across a range of deposition thickness (left) and yttrium silicate films (right) after annealing in air at 900 °C.

UV-Vis spectroscopy of the annealed silicate films indicated high optical transmittance across the 300-1600 nm wavelength range (Figure 4-14). Films under 70 nm exhibited a transmittance > 94% across the entire tested range, while 140 nm films were >90% transmissive at wavelengths over 400 nm.



Figure 4-14. Optical transmittance of yttrium silicate films after annealing in air at 900 °C.

XP spectra of yttrium-silicon films indicated that an increase in annealing temperature increased the proportion of yttrium silicate in the near-surface region of the material, as well as a decrease in presence of metallic silicate (Figure 4-15). Upon deposition, yttrium-silicon films were rich with metallic silicides, seen as a peak at ~98 eV. As annealing temperatures were increased to 500 °C, 700 °C, and 900 °C, the presence of silicides at 98 eV decreased, while a peak indicative of yttrium silicate at 101 eV increased in prominence, becoming the primary silicon oxidation state at the surface of the material.



Figure 4-15. XP spectra of yttrium-silicon films over a range of annealing temperatures. Vertical dotted lines indicate the literature values of SiO₂, silicates, and silicides.

Due to the predicted thermodynamic stability of yttrium silicate films, initial corrosion experiments indicated that metallic silicide films annealed at 900 °C inhibited the corrosion of the underlying silicon substrate. (Figure 4-16). SEMs indicated that the un-annealed yttrium-silicon film had entirely dissolved over the course of 24 hours, and the metallic silicide films annealed at 500 °C and 700 °C were heavily corroded. In contrast, films annealed at 900 °C showed no signs of chemical degradation over 1 day.



Figure 4-16. SEMs of yttrium silicate films after 1 day in 1 M KOH.

SEMs of silicate films annealed at 900 °C after exposure to 1 M KOH for over 2 days indicated that films catastrophically failed due to delamination from the substrate (Figure 4-17). SEMs indicated that the silicate films had rolled into tight cylinders, likely due to stresses formed in the silicate films during the annealing process. Oxygen uptake during oxidation of metallic silicide films causes the film to expand, introducing stresses. For this reason, the deposition method was altered to reactive sputtering in a mixed argon/oxygen plasma, which directly deposits an oxidized film (Scheme 4-1).



Figure 4-17. SEMs of 900 °C annealed yttrium silicate films after exposure in 1 M KOH for over 2 days.

4.4.2 Preparation of Low Impurity KOH

Platinum is a low overpotential catalyst for HER in both acidic and alkaline environments, and is the catalyst of choice for grid-scale PEM electrolyzers.¹⁹ For PEC devices, where catalyst loadings are limited, platinum can suffer from fouling over time. In 1 M KOH made from semiconductor grade pellets, the overpotential required to drive -10 mA/cm² of current density on a platinum disk electrode rapidly increases from the initial value of -180 mV up to -700 mV vs. RHE (Figure 4-18).



Figure 4-18. The overpotential required to drive -10 mA/cm² of current density over a platinum disk catalyst in as mixed 1 M KOH.

Visual comparison of Pt disks before and after use as a hydrogen evolving cathode in 1 M KOH shows that the Pt becomes fouled, with a notable change in color from a lustrous silver to a yellow-brown hue (Figure 4-19a). XPS analysis of the surface of a platinum electrode fabricated by sputtering metallic platinum onto a n^+ -Si substrate indicated that the surface was fouled with a substantial amount of Cu and Fe, which are known impurities in KOH. (Figure 4-19b-e). Due to

the cathodic current being flowed through the platinum electrode, metals ions in solution are driven to electrodeposit on the Pt surface, thereby reducing the catalytic activity of the surface. Although Ni is present in the KOH as a trace impurity in similar concentration of Cu and Fe, no Ni was observed on the electrode surface.



Figure 4-19. a) Picture of platinum disk electrodes before (left) and after (right) being used as a cathode for hydrogen evolution in 1 M KOH. XP spectra of an electrode of platinum sputtered onto a n⁺-Si substrate in the b) Pt 4f region, c) Cu 2p region, d) Fe 2p region, and e) Ni 2p region.

ICP-MS measurements of the KOH indicated that as-mixed semiconductor grade 1 M KOH contained Fe, Ni, and Cu impurity concentrations of 22 ppb, 44 ppb, and 3.5 ppb, respectively. A common method of reducing the concentration of metal ions in solution is preelectrolysis, which is applying 2-3 V between two graphite, carbon, or platinum electrodes in the KOH solution, which electrodeposits some of the impurity ions on the cathode surface. A preelectrolysis procedure with two Pt mesh electrodes in a small 50 mL batch of KOH showed the concentration of Fe, Ni, and Cu to decrease to 6.5 ppb, 2.8 ppb, and 0.4 ppb, respectively. Others have reported the utilization of a Ni(OH)₂ to precipitate Fe impurities out of solution, at the expense of drastically increasing the concentration of Ni ions in solution.¹⁶⁰ Treating as-mixed SC grade 1 M KOH with the aforementioned Ni(OH)₂ precipitation procedure reduced the Fe and Cu concentrations to 1.4 ppb and < 0.06 ppb, respectively. The Ni concentration after Ni(OH)₂ treatment increased substantially to 2500 ppb. Following the Ni(OH)₂ procedure with a pre-electrolysis step reduced the Ni concentration down to 5.5 ppb, at the expense of increasing the Fe and Cu concentrations slightly to 1.5 and 0.1 ppb, respectively. A summary of the impurity concentration after treatment steps is shown in Table 4-2.

Table 4-2. Summary of impurity Fe, Ni, and Cu metal concentration in 1 M KOH before and after various pretreatment procedures.

Impurity	As mixed (ppb)	Pre-electrolysis	Ni(OH) ₂	Ni(OH) ₂ then pre-
		(ppb)	treatment (ppb)	electrolysis (ppb)
Fe	21.8	6.5	1.4	1.5
Ni	44.3	2.8	2500	5.5
Cu	3.5	0.4	< 0.06	0.1

In addition to rigorously cleaning the KOH of metal impurities, the surface area of the catalyst was greatly enhanced by electrodepositing additional Pt onto the electrode surface. SEMs of silicon electrodes photolithographically decorated with 3 μ m Pt islands spaced by 7 μ m, followed by the further Pt electrodeposition of -800 mC/cm² of cathodic charge density show mushroom shaped islands of Pt that are ~4 μ m in diameter (Figure 4-20a). These patterned electrodes were utilized to measure the overpotential required to pass -10 mA/cm² of cathodic current density in 1 M KOH that had been pre-treated with the previously discussed techniques (Figure 4-20b).



Figure 4-20. A) SEM of Si electrode photolithographically patterned with Pt islands, followed by electrodeposition of Pt by passing 800 mC/cm² of cathodic charge density. B) Overpotential required to drive -10 mA/cm² of cathodic current through Pt-coated electrodes in panel A in 1 M KOH that had been pre-treated with pre-electrolysis only (red), or with a Ni(OH)₂+pre-electrolysis clean.

Utilizing a platinum disk electrode, which is flat and nearly featureless, in untreated 1 M SC grade KOH caused the overpotential required to drive -10 mA/cm² of current density to increase from the initial value of -180 mV up to -700 mV. Treating the KOH with a pre-electrolysis procedure, as well as patterning the electrode surface with a high surface area platinum catalyst, allowed the overpotential to remain more stable over multiple days of electrolysis, reaching a final plateau of -280 mV vs. RHE. By further pre-treating the KOH with the Ni(OH)₂ cleaning method followed by pre-electrolysis, further enhanced the overpotential. After 2 days of operation in the least impure KOH, the overpotential reached a steady value of -200 mV vs. RHE.

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