Solar Energy Storage Using Earth-Abundant Materials

Link Energy Fellowship Final Report

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1. Narrative

Introduction.

Among alternative energy technologies, solar is well suited to meet the grand energy challenge ahead if we can overcome the intermittent supply of sunlight.[1,2] Storing solar energy in chemical bonds serves as an attractive technical solution that requires selecting suitable chemical reactions and building tailored systems.[3] Many research groups are aiming to electrochemically reduce carbon dioxide to a solar fuel, such as ethanol, or split water into hydrogen and oxygen gas, but these groups have been unable to design efficient and cheap systems that navigate these complex multi-step chemical transformations without encountering significant parasitic overpotentials.[4] While we fully expect further advances to eventually solve these issues, in the intervening time parallel investigations should also focus efforts on alternative reactions, which more immediately address the growing demand for continuously supplied clean energy.

The vision of the system we have requires complete integration of light collection by a semiconductor made from abundant materials, efficient conversion of solar energy facilitated by inexpensive catalysts, and storage of the energy by reversible chemical reactions matched to the light absorber of interest. The aim of our work is to perform experiments that could lead to such a device, and in the process, advance the field of artificial photosynthesis as a whole. Our project began by the simulation and modeling of different materials and reactions to identify a candidate semiconductor and chemical reaction combination to more closely explore. Then, we identified a candidate cathode catalyst material, constructed a prototype photocathode assembly, and finally, initiated work on the photoanode. We hypothesized that hydrobromic acid splitting driven with two illuminated silicon electrodes would serve as an appropriate goalpost.

Results.

System architecture.

Simulation and modeling were used to study different scenarios to select the most promising combination of readily available semiconducting materials and reactions. For example, these simulations reveal that, in an obtainable system using one light absorber to simultaneously drive both oxidation and reduction reactions, water splitting could obtain a solar-to-hydrogen (η_{STH}) efficiency of up to 9 % for a single light absorber with a band gap of 2.3 eV, whereas splitting of hydrobromic acid into bromine and hydrogen (2HBr + Light → H_2 + Br_2) could obtain η_{STH} = 16 % for a band gap of 1.8 eV. More efficient designs using two light absorbers, configured to operate either in parallel (side-by-side) or in series (stacked), would use one semiconductor as a photocathode (driving the reductive half-reaction) and use the other semiconductor as the photoanode (driving the oxidative half-reaction). Realistically, a device using two 1.3 eV band gap materials in a side-by-side design could give η_{STH} = 14 % for water splitting, whereas two silicon photoelectrodes sitting side-by-side could reach η_{STH} = 17 % for hydrobromic acid splitting. The highest possible efficiency was achievable by using two materials that were stacked. For example, water splitting could best η_{STH} = 19 % and HBr splitting would see η_{STH} = 22 %. Unfortunately, building a stacked system (where light is partially transmitted through the top absorber) is difficult to construct. Given our laboratory's expertise with silicon, we could feasibly build two separate silicon photoelectrodes and connect them in parallel via an ohmic backside contact. In fact, in the 1970s Texas Instruments pursued a similar system using silicon in a side-by-side fashion to split hydrobromic acid, but they used expensive Pt/Ir as a dual-purpose protective and catalytic layer.[5]

Photocathode assembly.

Platinum is one of the most active inorganic electrocatalysts for the hydrogen evolution reaction (2H^+ + 2e^- → H_2), but it is too expensive. Previous work in our group has observed metal phosphides displaying promising activity and stability in highly acidic solutions, such as CoP.[6,7] While metal phosphides did not demonstrate supreme tolerance of bromine, the only requirement for the cathode catalyst is prolonged acidic stability. An intervening and already-required proton selective membrane (Nafion) could allow for passage of protons and prevent poisoning by

bromine.[8] Having selected a suitable catalyst and semiconductor, our attention was turned to the integration of these materials into a working photocathode.

Cheap materials, such as CoP, require high mass loadings to meet desired performance metrics, but thick layers of catalyst will block light from reaching an underlying planar light collector. We decided to beat this limitation by structuring the underlying semiconductor into silicon microwires that were 4 µm in diameter, 11 µm in pitch, and 50 µm tall by reactive ion etching of a Si(100) substrate. Vapor diffusion of phosphorous gave a radial emitter that was necessary for generating photovoltage. Our pn^+ radial-junction silicon microwires were coated by centrifugation of a CoP nanoparticle suspension to create a thick layer of the catalyst at the base of the microwire array. For a comparison, Pt nanoparticles were also synthesized and deposited in the same fashion. The CoP-coated photocathode exhibited an ideal regenerative-cell efficiency of 1.9 %, but the Pt-coated photocathode achieved 2.9 %. The lower efficiency seen by the CoP was due to a resistance putatively assigned to a relatively poor electrical contact between the nanoparticles and the silicon, but this limitation was resolved by electrodepositing CoP, thereby increasing the efficiency of the CoP-coated photocathode to 4.0 %. The improved photocathode outperformed the extrinsic performance of Pt under our tested conditions, but this is not to say we cannot build more efficient Pt-coated devices. This photocathode appeared suitable for our proposed system, therefore allowing our attention to be directed at the photoanode.

Photoanode.
A silicon photocathode is reductively stable in acidic solutions, but silicon thermodynamically favors forming an undesirable passivating oxide in aqueous solutions under oxidative conditions and requires suitable protection from oxidation. Previously in our group,[9] we transferred single graphene crystals onto n-type silicon to make photoanodes that could sustain oxidation of ferrocyanide, but the process was tormented by unknown factors leading to batch-to-batch variability in the endurance of tested photoanodes. The leading hypothesis offered was that varying defect densities in the graphene were susceptible to chemical attack, giving some electrodes with a low defect density superior performance over electrodes with a higher defect density. We were able to test a silicon n-type photoanode for the oxidation half-reaction required for the HBr splitting ($2Br^- \rightarrow Br_2 + 2e^-$) protected by graphene, and it displayed promising

stability and activity on one electrode, but we were ultimately prevented from further investigation due to the irreproducibility of the process. Instead, we turned our attention to passivating these reactive defect-sites in graphene with XeF_2 to fluorinate our graphene by the passivating defect sites with C-F bonds. Unprotected n-type silicon electrodes decay in HBr solutions within seconds of initiating photoactivity, but n-type silicon protected by lightly fluorinated graphene appeared significantly more stable and efficient than bare silicon. In order to obtain an ideal regenerative-cell efficiency of 3.5 % required a Pt catalyst. Unfortunately, our high photoanode activity depended on finding a non-precious metal anode electrocatalyst, leading us to visit different materials for catalysts of the anode.

Anode materials.

We had initially hoped CoP would act as an efficient anode catalyst, but these materials did not display prolonged reliability required in an anode for the oxidation of bromide (although the metal phosphides have been used as effective precursors to oxygen evolution catalysts). We investigated the use of pulsed-laser ablation in liquids for the synthesis of complex nanominerals but were unsuccessful in the search for a stable anode catalyst material for halide oxidation.

Significance and impact.

We successfully elevated the field as a whole and made significant progress towards construction of our envisioned system. Our team wrote and released a review paper, in part to review investigations inspired by our work with metal phosphides, and also to educate the materials research community on key metrics and experimental aspects missed in some reports. We believe this ultimately has had a positive impact on the community's best practices and have been pleased with the significant advancements made by the community in improvements to metal phosphides (and derivatives) for the hydrogen evolution reaction. The photocathode prototype inspired a number of publications that successfully improved upon these devices to make promising prototypes to be used in water splitting systems.[10-12] These initial systems are key milestones required for gaining industrial interest. One of the current active foci of the research community is on improving the photoanode, where many different strategies are being pursued simultaneously. Our research team significantly improved a process using graphene as a

protective layer for photoanodes, leading the way to use 2D materials as protection layers in electrochemical systems.

Where might this lead?

We believe this work has demonstrated that electrocatalysts made from earth-abundant materials can compete with precious metal materials, potentially lowering the economic barrier to building a future energy system that stores solar energy in the form of chemical bonds. The key determinants for using these materials in real systems is their long-term stability, complexity in manufacturing, associated costs, and economic demand at the price point available. We hope these materials, or derivatives thereof, will be evaluated for use in a real system. Ultimately, we cannot depend on fossil fuels forever, and we will need to use different energy sources that are more sustainable, given the scale of our energy demands, but even once the technological solutions are solved there are still substantial barriers to their implementation remaining.

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2.   List of publications acknowledging the support of the Link Foundation Fellowship:

- "Comparison of the Performance of CoP-Coated and Pt-Coated Radial-Junction n^+p-Silicon Microwire-Array Photocathodes for the Sunlight-Driven Reduction of Water to $H_2(g)$". C.W. Roske; E.J. Popczun; B. Seger; C.G. Read; T. Pedersen; O. Hansen; P.C.K. Vesborg, B.S. Bruncshwig, R.E. Schaak; I. Chorkendorff; H.B. Gray; N.S. Lewis. *J. Phys. Chem. Lett.*, **2015**, *6*, 1679-1683.
- "Lightly Fluorinated Graphene as a Protective Layer for n-Si(111) Photoanodes." A.C. Thompson; A.C. Nielander; C.W. Roske; J. Maslyn; J. Hao; N. Plymale; J. Hone; N.S. Lewis. *Nano Lett.*, **2016**, *16*, 4082-4086.
- "Synthesis, Characterization, and Integration of Metal Phosphide Catalysts for the Hydrogen Evolution Reaction." J. Callejas; C.G. Read; C.W. Roske; N.S. Lewis; R.E. Schaak. *Chem. of Mater.* **2016**, *28*, 6017-6044.
- "Complex Nanomineral Formation Utilizing Kinetic Control by PLAL." C.W. Roske; J.W. Lefler, A.M. Muller. *J. Colloid and Int. Sci.* **2017**, *489*, 68-75.

3. Impact of Fellowship

I am grateful for the opportunities and intellectual freedom afforded to me during and after my tenure of this prestigious fellowship. I was able to take on an ambitious research project, where I worked towards the device described here. Our work on the metal phosphides has been received with significant interest by the entire field of artificial photosynthesis, with these materials being successfully studied for application in systems ranging from water splitting, carbon dioxide reduction, and more. The support offered by the fellowship was crucial during my most productive years in graduate school and prepared me well for the work I am now employed to do and plan to do during my career.