Supporting Information

An Experimental and Modeling/Simulation Based Evaluation of the Efficiency and Operational Performance Characteristics of an Integrated, Membrane-Free, Neutral pH Solar-Driven Water-Splitting System

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Analysis of gas composition

When pure H_2 was injected for the GC analysis (Run#9 and Run#65) using the same sample collection procedures as the gaseous product analysis in this study, 3~5% air was found in the O_2/N_2 channel, which contributes to the baseline of all the gas composition analyses.

When pure O_2 or air was injected for the GC analysis (Run #7, 64 and Run #8, 63), minimal other gas contaminants were detected.

For well-sealed devices with membranes, minimal product-gas crossover was observed (Run #16 and Run #18).

For devices with membranes that were not well-sealed, and where some tiny pin-holes were present along the edge of the PEC chip, the crossover increased significantly (Run #4 and Run #10)

GC Run (#)	Sampled from:	Time (min)	H_2 (%)	O_2 (%)	N_2/air (%)
4	O_2		93 (10)	852 (59.2)	310 (28.2)
7	Pure O_2			1321 (100)	
8	Air			287 (0)	1108 (100)
9	Pure H_2		956 (95)	15 (0)	60 (5)
10	H_2		526 (55)	173 (4.7)	444 (40.3)
16	O_2		30 (3.2)	479 (20.7)	846 (76.9)
18	H_2		252 (26.8)	184 (0)	815 (74.1)
63	Pure air			283 (0)	1093 (100)

			31 (0)	1289 (100)	13 (0)
64	Pure O_2				
			892 (97)	9 (0)	36 (3)
65	Pure H_2				

Effect of Catalyst Deposition on STH Conversion Efficiency

Photodeposition of the Co-Pi oxygen-evolution catalyst onto the 3J a-Si:H photovoltaic cell was straightforward and reproducible. STH efficiencies of ~ 2% were readily achievable when this approach was used. Deposition of the catalyst was accomplished in "horizontal" or "vertical" orientation during deposition, and either thick gray-blue film or thin light-blue film could be obtained by simply varying deposition time.

A specific method for catalyst deposition allowed our devices to achieve even higher (>3%) STH efficiencies. Specifically etching a thick, vertically deposited Co-Pi film with a drop of diluted (10mM) H_2SO_4 greatly improved the STH efficiency. Although sometimes a device appeared "dead", in that the STH efficiency decreased significantly and OER catalyst turned white-gray in color, after operation for several hours the H_2SO_4 etching treatment could completely restore the efficiency as well as the appearance of the device. One such example is shown in Figure 2(b), where a 60 s etch was applied after 600 min of operation when the device appeared "dead". By carefully controlling the etch time, the Co-Pi film could be completely removed without damaging the 3J a-Si:H material. The deposited Co-Pi film also sometimes developed cracks and pieces of the film fell off of the electrode. Most of the devices performed well continuously for a several to tens of hours. Based on our observations, we believe loss of catalyst, plating of impurities on the anode and/or cathode and corrosion of etched edges

of 3J a-Si:H PV materials are the main sources for the decrease of the systems efficiency over the time of operation.

Although the performance of the Ni-Mo hydrogen-evolution catalyst was comparable to that of the Pt hydrogen-evolution catalyst over a short duration, the performance of the Ni-Mo catalyst degraded more quickly in the 1 M KBi (pH=9.2) solution than did the performance of the Pt catalyst.

Product Crossovers

Although low product-recombination losses ($< 5\%$) were observed in the membrane-free system, the product-gas crossovers exceeded the flammable limit (4 vol.%) of the hydrogen gas and oxygen gas mixture. In the membrane-free system, dissolved gases should reach saturation and be well mixed in both sides of the reaction chamber, while undissolved species have to partition out of the liquid phase. The undissolved molecules can evaporate at the liquid-gas interface if sizeable head space is present in each compartment, or alternatively the undissolved molecules could join a bubble that had already formed, or could nucleate on the interior wall surfaces which provided a large interface for gases to form bubbles and escape. In our experiments, the size of head space was minimized, and gases were removed as quickly as possible from the system. The effect of varying the head space was also experimentally verified, for example, the percentage of O_2 in gases collected from the cathode compartment could be doubled if a large head space was allowed. Gas molecules readily joined existing bubbles, but this crossover mechanism was insignificant in our system because most bubbles formed near the catalytic surfaces. Therefore, we believe the main route for gaseous products to enter the opposite side of the device was through the interior wall

surfaces, which could be significantly reduced in an optimal design. In the current cell design, the ratio between the catalytic surface area and the interior wall surface area was ~ 1:10. As a result, a few bubbles from the wall surface would easily affect the gas purity. This effect was observed frequently, as can be seen, for example in Figure 4, where the H_2 concentration increased precipitiously to 40% in anode compartment. Other researchers have reported similar observations[1]. Fortunately, many engineering techniques are capable of significantly reducing this effect.

1.   S. Y. Reece, J. A. Hamel, K. Sung, T. D. Jarvi, A. J. Esswein, J. J. H. Pijpers and D. G. Nocera, *Science*, 2011, **334**, 645-648.