Modeling a Coupled Photovoltaic-Photoelectrochemical (PV-PEC) System for Hydrogen Generation

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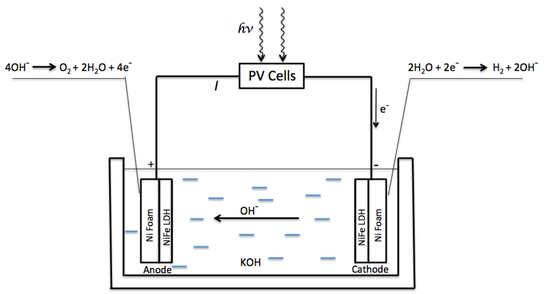
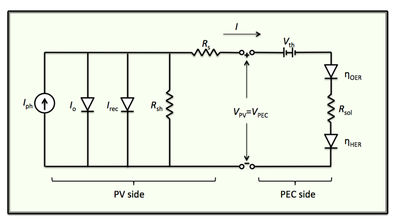
Motivation and Goal

Direct conversion of solar energy into storable fuels is considered one of the most promising energy technologies of the future. However, finding a good material for this cause is one of the major challenges in this area. NiFe layered double hydroxide (LDH) films have attracted enormous attention owing to their high activity toward both Oxygen Evolution Reaction (OER) and Hydrogen Evolution Reaction (HER)[1], as well as their low cost, simple preparation methods and earth abundance[2]. In this research, we consider NiFe LDH as both OER and HER electrodes, with a goal of understanding the mechanism and kinetics of the OER and HER on the electrode, using combined modeling and experimental procedure.

System Description



PV-PEC coupled system



Equivalent circuit of the coupled system

PV-PEC Operating conditions

For an M (parallel) × N (series) identical c-Si PV cells, the the output current can be represented as

$$I = M\left\{ -I_{ph} + \left(I_o - qx_{Si}Bn_i^2\right)\exp\left(q\frac{V/N-(I/M)R_s}{\beta k_B T}\right) + \frac{V/N-(I/M)R_s}{R_{sh}}\right\}$$

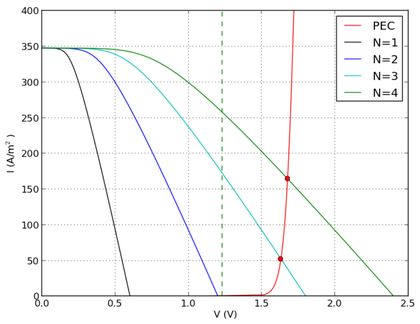
For direct coupling of the PV-PEC cells

$$V_{PV} = V_{PEC} = \mu_{th} + \eta_{OER} + \eta_{HER} + IR_{sol}$$

The Tafel equation provided below is used for the OER and HER electrodes overpotentials

$$\eta = 0.04 \times \log\left(\frac{I}{5.62\times10^{-4}}\right)$$

where 0.04 V and 5.62×10^{-4}A/m^2 are the Tafel slope, and the exchange current density, respectively [3].



I vs V curve for M=1

OER Reaction Network Analysis

In basic media, the net cell reaction is

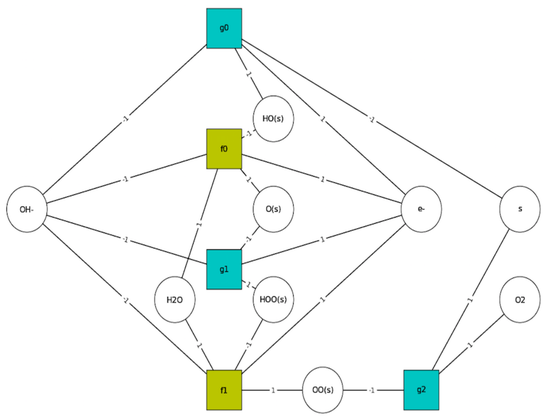
$$2\,H_2O\,(l) \longrightarrow 2\,H_2(g) + O_2(g) \quad E^o_{cell} = -1.23\,V$$

For the OER, the surface reactions mechanism is

$$S + OH^- \longrightarrow OH + e^-$$
$$OH + OH^- \longrightarrow O + H_2O + e^-$$
$$O + OH^- \longrightarrow OOH + e^-$$
$$OOH + OH^- \longrightarrow OO + H_2O + e^-$$
$$OO \longrightarrow O_2 + S$$

The net half reaction is

$$4\,OH^- \longrightarrow O_2 + 2\,H_2O + 4\,e^- \quad E^o = -0.40\,V$$



Reaction network graph for OER

OER species balance

$$\frac{d\mathbf{m}}{dt} = \phi_1 \mathbf{R}^{n_s\times n_r}\mathbf{h}^{n_r\times 1}$$

where $\mathbf{m}$ represent the molar amount of each species

$$\frac{d}{dt}\begin{bmatrix} OH^-_{(aq)} \\ S \\ OH \\ O \\ OOH \\ OO \\ O_{2(aq)} \\ e^- \\ H_2O_{(aq)} \end{bmatrix} = \phi_1 \begin{bmatrix} -1 & -1 & -1 & -1 & 0 \\ -1 & 0 & 0 & 0 & 1 \\ 1 & -1 & 0 & 0 & 0 \\ 0 & 1 & -1 & 0 & 0 \\ 0 & 0 & 1 & -1 & 0 \\ 0 & 0 & 0 & 1 & -1 \\ 0 & 0 & 0 & 0 & 1 \\ 1 & 1 & 1 & 1 & 0 \\ 0 & 1 & 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} \frac{1}{\epsilon}g_0 \\ f_0 \\ \frac{1}{\epsilon}g_1 \\ f_1 \\ \frac{1}{\epsilon}g_2 \end{bmatrix}$$

Factorization procedure

a) Fast Modes:

$$\frac{d}{dt}(S - O_{2(aq)}) = -g_0/\epsilon$$
$$\frac{d}{dt}(-OH^-_{(aq)} + 2S + OH - OO - 3O_{2(aq)}) = g_1/\epsilon$$
$$\frac{d}{dt}(O_{2(aq)}) = g_2/\epsilon$$

b) Slow Modes:

$$\frac{d}{dt}(S + OH - O_{2(aq)}) = -f_0$$
$$\frac{d}{dt}(OO + O_{2(aq)}) = f_1$$

c) Instantanious Modes:

$$OH^-_{(aq)} + OH + O + 2OOH + H_2O_{(aq)} + 2OO + 2O_{2(aq)} = w_0$$
$$OH^-_{(aq)} + OH + OOH + 2H_2O_{(aq)} = w_1$$
$$S + OH + O + OOH + OO = w_2$$
$$OH^-_{(aq)} + e^- = w_3$$

where w is a constant corresponding to a conserved quantity.

References

[1] Luo, J. *et al.* (2014). Water photolysis at 12.3% efficiency via perovskite photovoltaics and Earth-abundant catalysts. *Science (New York, N.Y.), 345*(6204), 1593-6.

[2] Lu, Z. *et al.* (2014). Three-dimensional NiFe layered double hydroxide film for high-efficiency oxygen evolution reaction. *Chemical Communications (Cambridge, England), 50*(49), 6479-82.

[3] Ma, W. *et al.* (2015). A superlattice of alternately stacked Ni-Fe hydroxide nanosheets and graphene for efficient splitting of water. *ACS Nano, 9*(2), 1977-84.

Conclusion and Future Work

The use of NiFe LDH as an active material for OER and HER is relatively new to the field, and the mechanisms occurring at these electrodes are still not fully understood. This project will help to clarify the OER and HER reaction kinetics and mechanism on the NiFe LDH electrodes.

We are in the process of synthesizing NiFe LDH on Ni foam substrate and test the electrodes experimentally in Hofmann voltameter apparatus. In addition, Electrochemical Impedance Spectroscopy (EIS) will be performed on the electrodes to identify the equivalent electrical circuit diagram components and correlate them with some of the reaction rates constants unrevealing the kinetics of the individual reaction steps. The reaction rate constant can aid to estimate the species concentration profile on the electrodes.

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