Supporting Information

Sixteen Percent Solar to Hydrogen Efficiency Using a Power Matched Alkaline Electrolyzer and a High Concentrated Solar Cell: Effect of Operating Parameters
Shahid M. Bashir, Muhammad A. Nadeem, Maher Al-Ofi, Mohannad Al-Hakami, Tayirjan T. Isimjan, Hicham Idriss*

Hydrogen Platform, SABIC Corporate Research and Development Center, KAUST, Thuwal 23955, Saudi Arabia

Solar Cell Assembly (SCA)

Figure S1. Diagram of a solar cell assembly (SCA)
Solar concentration

Figure S2. Sketch of SCA describing the parameters used to obtain the sun concentration.

The * indicates the no. of sun before taking into account the optical efficiency of Fresnel lens (85%). The optical efficiency was estimated from the transmittance spectrum of the Fresnel lens obtained from the manufacturer Edmund Optics (http://www.edmundoptics.com). This value equals to 218 after the correction. The ** shows the possible no. of sun if the light is homogenous and cover the area of 0.49 cm², while *** indicates the no. of sun if the light guide (or secondary optics) with a similar geometry as the PV cell is used. Further elaboration is provide below.
The concentration of sun light or number of sun is the ratio of geometric area of uniform input solar flux (Fresnel lens area) and the area of uniform concentrated spot at solar cell, Eq. S1. Solar concentration can also be determined using the ratio of short circuit current at high concentration to the short circuit current generated by solar cell at non-concentrated light (1 sun), Eq. S2.

Number of sun based on geometric area = \frac{\text{Area of solar flux receiver (Fresnel lens)}}{\text{Area of spot at solar cell}} \quad S1

Number of sun based on current = \frac{\text{Isc at concentrated light}}{\text{Isc at one sun}} \quad S2

Ideally, a concentrated sunlight area should fully cover the solar cell. In this case, when the size of receiving area is larger than the solar cell area, sun concentration can be calculated based on the input flux on the solar cell area, rather than the geometric area of the spot to evaluate the cell performance. As shown in Fig. S2, the measured concentrated spot size of 5 cm diameter was recorded at an arbitrary position, then using symmetry principles, the actual number of sun is calculated using Eqs. S3 and S4. The Fresnel lens used in current study has a diameter of 20 cm, which corresponds to 314 cm², while the size of solar cell is 0.316 cm² with a square dimensions of 0.562 cm.

\frac{\text{Fresnel lens area}}{\text{Measured spot area}} = \frac{\text{Measured spot area}}{\text{Actual spot area on PV cell}} \quad S3

\frac{\text{Fresnel lens area}}{\text{Actual spot area on PV cell}} = \text{Number of sun} \quad S4

The theoretical possible spot (circular) needed to cover the entire solar cell is 0.49 cm² which could provide about 640 suns based on geometric area as described above. However, due to the absence of the secondary optics, maximum sun concentration obtained at a spot position is around 256 at a controller power of 1000 with a spot area of 1.228 cm². The controller power of 1000 corresponds
to 1 sun. Based on the solar concentration of 256 x at a spot area of 1.228 cm$^2$ and the optical efficiency of the Fresnel lens (85%) the actual sun concentration on the solar cell (0.316 cm$^2$) is about 218 sun.

**Alkaline Electrolyzer Setup**

![Figure S3. Setup of an alkaline water electrolysis system. Photo taken by authors.](image)

The performance of an alkaline electrolyzer was obtained by carrying out chronoamperometric measurement at different set potentials. The reaction time of 1000 sec was sufficient to provide the steady state current values. Hydrogen and oxygen gases were also measured during each chronoamperometric run. The efficiency of water electrolyzer was calculated using Eqs. S5-S8.

**Electrolyzer Efficiency**

Electrolyzer Efficiency = (η) = Faradaic Efficiency x Voltage Efficiency  

S5

The faradaic and voltage efficiency of the system can be written as
Faradaic Efficiency (\%) = F.E. = \frac{\text{Charge used}}{\text{Charge passed}} = \frac{n_{\text{Fe}}}{I_{\text{opt}}} \quad \text{S6}

Voltage efficiency (\%) = V.E. = \frac{\text{Thermodynamic Voltage}}{\text{Operating Voltage}} = \frac{1.23 \times \text{(LHV)}}{V_{\text{op}}} \quad \text{S7}

Electrolyzer Efficiency(\%) = (\eta) = \frac{n_{\text{Fe}}}{I_{\text{opt}}} \times \frac{1.23}{V_{\text{op}}} = \frac{P(H_2)}{P_{\text{op}}} \quad \text{S8}

Where F = Faraday’s constant = 96487 C/mol, e = No. of electron for H\(_2\) formation = 2, I_{\text{op}} = \text{Operating current (A)}, V_{\text{op}} = \text{Operating voltage (V)}, t = \text{Reaction time (sec)}, n = \text{Moles of H}\(_2\) = \frac{PV}{RT}, P = \text{Pressure} = 1 \text{ atm} = 101325 \text{ Pa or kg/(m-s\(^2\))}, T = \text{Absolute temperature (K)}, V = \text{Volume of Hydrogen (L)}, R = \text{Gas constant} = 8.314 \text{ J/mol/K}, P(H_2) = \text{Power to hydrogen} = \text{moles of hydrogen} \times \text{LHV}, P_{\text{op}} = \text{Operating power} = I_{\text{op}} \times V_{\text{op}}, \text{LHV} = \text{Lower heating Value (1.23 V or 237000 J/mol)}. 
**Figure S4.** Chronoamperometric curves (I-t) generated under 1 M KOH at 23 °C at electrode area of (a) 0.25 cm$^2$ (b) 0.5 cm$^2$ (c) 2.0 cm$^2$ and (d) 4.5 cm$^2$.

**Table S1.** No. of active sites (moles x Avogadro No.) of NiFe$_2$O$_4$ anode catalyst in different electrode areas

| Electrode Area (cm$^2$) | Loading (2 mg/cm$^2$) | Mass of catalyst (mg) | Mass of catalyst (g) | No. of moles | No. of active sites |
|-------------------------|-----------------------|-----------------------|----------------------|--------------|-------------------|
| 0.25                    | 2                     | 0.5                   | 0.0005               | 2.13 x 10$^{-6}$ | 1.3 x 10$^{18}$   |
| 0.5                     | 2                     | 1                     | 0.001                | 4.26 x 10$^{-6}$ | 2.6 x 10$^{18}$   |
| 2                       | 2                     | 4                     | 0.004                | 1.70 x 10$^{-5}$ | 1.0 x 10$^{19}$   |
| 4.5                     | 2                     | 9                     | 0.009                | 3.83 x 10$^{-5}$ | 2.3 x 10$^{19}$   |
Electrolyzer overpotential derivation

Due to irreversibility of various processes in an electrolyzer, the operating voltage ($V_{op}$) is always higher than the reversible water splitting voltage (1.23 V; $V_{rev}$) at STP. It is also higher than the thermoneutral voltage (1.48 V; $V_{th}$), if the electrolyzer works close to adiabatic conditions, (heat introduction can be neglected). The $V_{op}$ is calculated from:

$$V_{op} = V + \eta$$

where $\eta$ is an irreversible voltage contribution to $V_{op}$ and includes ohmic potential losses ($\eta_{ohmic}$), concentration potential losses ($\eta_{conc}$) and activation potential losses ($\eta_{act}$). As activation potential losses are fixed for a given electrocatalyst and its loading, it can be written as:

$$\eta = \eta_{ohm} + \eta_{conc}$$

$\eta_{ohm}$ are due to ionic resistance ($R_{ion}$) and electronic ($R_{elec}$) resistance. $R_{elec}$ is due to current collectors and other metal parts. $R_{ion}$ is due to solid electrolyte (membrane electrode assembly; MEA).

$$\eta_{ohm} = IR_{ion} + \eta_{elec}$$

$R_{elec}$ can be neglected due to much lower resistance of metals ($10^{-3}$-10$^{-7}$ ohm) than solid electrolyte (10-10$^{-3}$), where $I$ is the current

$$\eta_{ohm} = IR_{ion}$$

Resistance is characteristic of size, shape, and material properties such that $R_{ion} = \frac{L}{\sigma A}$. Where $L$, $A$, and $\sigma$ are thickness, surface area, and conductivity of MEA. Since $I = j * A$, Eq. S13 is obtained for $\eta_{ohm}$ after substituting $I$ and $R_{ion}$ into Eq. S12:

$$\eta_{ohm} = \frac{IL}{\sigma A} = \frac{jL}{\sigma}$$
For a given electrolyzer, $\eta_{\text{ohm}}$ increases with an increase in $j$ (current density) or a decrease in MEA area at constant $I$.

When $j$ is low and the bulk OH\textsuperscript{-} concentration is high, the $\eta_{\text{conc}}$ is not important, but under high $j$ and lower OH\textsuperscript{-} concentration, $\eta_{\text{conc}}$ become critical. The $j$ for an electrolyzer can be calculated using Eq. S14\textsuperscript{1}.

$$
 j = \frac{nFD(C^* - C(x\to0))}{\delta_0} \tag{S14}
$$

where $C^*$, $C(x\to0)$, D, n and $\delta_0$ are bulk and surface concentrations of OH\textsuperscript{-}, diffusion coefficient, number of electrons transferred per mole and Nernst diffusion layer thickness, respectively. When $c(x = 0)$ falls to zero, a limiting current density ($j_L$) situation is established.

$$
 j_L = \frac{nFDc^*}{\delta_0} \tag{S15}
$$

Dividing eq. 6 by eq. 7:

$$
 1 - \frac{j}{j_L} = \frac{C(x\to0)}{c^*} \tag{S16}
$$

The Nernst equation in the absence of any current flow is ($c(x\to0) \gg c^*$):

$$
 E_{I\to0} = E^o + \frac{RT}{nF}\ln C^* \tag{S17}
$$

The Nernst equation when current flows is ($C^* \gg C(x\to0)$):

$$
 E = E^o + \frac{RT}{nF}\ln C (x\to0) \tag{S18}
$$

The potential difference ($\Delta E$) due to concentration change at the electrode is $\eta_{\text{conc}}$:

$$
 \Delta E = \eta_{\text{conc}} = \frac{RT}{nF}\ln \frac{C(x\to0)}{c^*} \tag{S19}
$$

Substituting eq. S16 into eq. S19:

$$
 \eta_{\text{conc}} = \frac{RT}{nF}\ln \left(1 - \frac{j}{j_L}\right) \tag{S20}
$$
\( \eta_{\text{conc}} \) is associated to both electrodes. It is to be noted that \( j_L \) of anode and cathode are different due to different type of reactants (OH\(^-\) for anode and H\(_2\)O for cathode in this case) involved.

\[
\eta_{\text{conc}} = \frac{RT}{nF} \ln \left( 1 - \frac{j}{j_{L,\text{anod}}} \right) + \frac{RT}{nF} \ln \left( 1 - \frac{j}{j_{L,\text{cath}}} \right)
\]  

S21

Combining Eqs. S9, S10, S13, and S21, Eq. S22 is obtained.

\[
V_{\text{op}} = V + \frac{j_L}{\sigma} + \frac{RT}{nF} \ln \left( 1 - \frac{j}{j_{L,\text{anod}}} \right) + \frac{RT}{nF} \ln \left( 1 - \frac{j}{j_{L,\text{cath}}} \right)
\]  

S22

The total \( V_{\text{op}} \) voltage can be calculated using Eq. S22.

SI References

[1] Bard, A.J.; Faulkner, L.R.; Leddy, J.; Zoski, C.G. Electrochemical methods: fundamentals and applications, wiley New York 1980.