Faradaic efficiency in protonic-ceramic electrolysis cells

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Abstract
Proton-conducting ceramics (e.g. doped barium zirconates or cerates) are typically mixed ionic-electronic conductors (MIECs). The electronic conduction, typically in the form of positively charged small polarons or electron holes, leads to ‘electronic leakage.’ In an ideal steam-electrolysis cell, one gas-phase H₂ molecule is produced from every two electrons delivered from an external power source. In other words, such ideal behavior achieves 100% faradaic efficiency. However, the electronic flux associated with MIEC membranes contributes to reduced faradaic efficiency. The present paper develops a model that predicts the behavior of faradaic efficiency as a function of electrolysis-cell operating conditions. Although the model framework is more general, the paper focuses on the behavior of a cell based upon a BaCe₀.₇Zr₀.₁Y₀.₁Yb₀.₁O₃₋δ (BCZYy) membrane. The study predicts the effects of operating conditions, including temperature, pressure, and gas compositions.

1. Introduction

Faradaic efficiency is widely used as a performance metric for protonic ceramic electrolysis cells. There is general agreement that faradaic efficiency is defined as

$$\eta_f = \frac{2FJ_{H_2}}{i},$$

where $J_{H_2}$ is net hydrogen molar flux (per cell area), $i$ is the externally imposed current density, and $F$ is the Faraday constant. Despite general, although not universal, agreement on the meaning of faradaic efficiency, there are significant qualitative and quantitative differences in published faradaic efficiencies [1, 2]. Some papers report that faradaic efficiency increases as the imposed current density increases, with vanishingly small faradaic efficiency near open-circuit conditions (cf [3–7]). Other papers report that faradaic efficiency decreases as imposed current density increases, with near-unity faradaic efficiency near open-circuit conditions (cf [8–12]). Such apparently contradictory reports potentially confuse the practical utility of faradaic efficiency as a performance metric.

In an ideal electrolysis cell, gas-phase H₂O(g) is dissociated on the posistrode to deliver protons OH⁺(el) to the protonic-ceramic electrolyte membrane, electrons to the external circuit and O₂(g) to the gas phase. Stated in Kröger–Vink notation,

$$2\text{H}_2\text{O}(g) + 4\text{O}_\text{O}^\text{el} \rightleftharpoons 4\text{OH}^\text{el} + 4\text{e}'(ed) + \text{O}_2(g),$$

where $O_\text{O}^\text{el}$ is a neutral oxygen site within the protonic-ceramic membrane, (el) and (ed) denote the electrolyte and electrode phases, respectively. Following proton transport through the protonic-ceramic membrane, the role of the negatrode is to consume electrons from the external circuit to produce the desired H₂. In Kröger–Vink notation,

$$2\text{OH}^\text{el} + 2\text{e}'(ed) \rightleftharpoons 2\text{O}_\text{O}^\text{el} + \text{H}_2(g).$$

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If the membrane were a pure proton conductor (i.e. not a mixed mixed ionic and electronic conductor (MIEC)), the processes represented by equations (2) and (3) would consume two electrons from the external circuit to produce one molecular hydrogen, yielding perfect faradaic efficiency.

However, because most protonic-ceramic electrolytes are MIECs, there is some ‘electronic leakage’ that serves to reduce faradaic efficiency. In other words, some of the imposed electrical current can be conducted through the membrane without producing proton flux, and hence hydrogen flux. The undesired electronic flux through the membrane is typically in the form of a small polaron or an electron hole. In BCZY (BaCe$_{1-x}$Zr$_x$Y$_2$O$_{3-δ}$) solid-solution electrolytes, increasing cerium content tends to increase faradaic efficiency. This is because the electrolyte electronic contributions decrease in oxygen-containing atmospheres [3, 15]. Han et al studied 20% yttrium-doped BCZY solid solutions with varying Ce content, ranging from BZY20 (BaZr$_0.8$Y$_{0.2}$O$_{3-δ}$) to BCY20 (BaCe$_{0.8}$Y$_{0.2}$O$_{3-δ}$) [15]. They reported an increase of the dehydration temperature with increasing the cerium content, ranging from 375 ± 25 °C to 625 ± 25 °C for BZY20 and BCY20 respectively. This result shows that the cerium component favors the stabilization of protons. Additionally, Han, et al determined transport numbers—first for the electronic contribution in oxidizing atmosphere and the ionic contribution. Increasing the cerium content leads to a decrease of the electronic transference number and an increase of the ionic one. The protonic and anionic (oxygen ions) contributions could be further distinguished. The ionic transport number is primarily protonic at 500 °C and 550 °C for all the compositions, independent of the cerium content. However, as temperature increases above 550 °C, the anionic contribution increases with the cerium content reaching 40% for BCY20 at 650 °C. Together with supporting DFT simulations, they concluded that the more favorable hydration thermodynamics for high cerium content is accompanied by reduced proton mobility. While higher cerium content is undesirable for stability in high steam environments, there is a compromise to be made. A BCZY solution with 40% of cerium on the perovskite B-site has proven to be stable in electrolysis mode [6]. An alternative approach could be to use a higher cerium containing BCZY such as BCZYb7111 (BaCe$_{0.2}$Zr$_{0.1}$Y$_{0.1}$Yb$_{0.1}$O$_{3-δ}$) and add a thin protective layer on the high steam side (for example a pyrochlore [11]).

In addition to properties of the electrolyte material itself, the faradaic efficiency depends on numerous operating conditions that include current density, temperature, pressure, and gas compositions on both sides of the membrane. Table 1 summarizes aspects of reported faradaic efficiencies. Higher steam pressures and lower temperatures diminish electronic conductivity, leading to higher faradaic efficiencies [6, 10, 16]. Because increasing the current density increases Joule heating, high current density can cause the electrolyte to be significantly higher than the furnace temperature. For example, assume an area specific resistance of ASR = 1 Ω cm$^2$ and an imposed current density of $i = 1$ A cm$^{-2}$. The resulting heat generation (per membrane area) owing to membrane polarization and proton flux is $Q \approx 1$ W cm$^{-2}$ [17]. As discussed subsequently, this could explain the decrease of faradaic efficiency with increasing the current density. Chemistry on steam-side electrode also impacts the hydrogen fluxes produced, and therefore the faradaic efficiencies. Higher performance electrodes lead to increased faradaic efficiency [6, 10].

**1.1. Faradaic efficiency characteristics**

Figure 1 illustrates the general behavior of faradaic efficiency as a function of imposed current density. In electrolysis, by convention, the imposed current densities are negative, making a distinction from fuel-cell operation. The gas-phase composition on the hydrogen-collection side is typically moist hydrogen. The gas-phase composition on the steam-feed side is typically a mixture of H$_2$O and O$_2$, which is the product of the steam dissociation. The behavior shown in figure 1 is based on operating at 600 °C and atmospheric pressure. The hydrogen-collection side is maintained at 97% H$_2$ and 3% H$_2$O. The steam-feed side is maintained as a steam-depleted composition with 80% O$_2$ and 20% H$_2$O.

Near open circuit, the faradaic efficiency decreases sharply, becoming negative at low current density. Based on the gas-phase compositions, there is always a high H$_2$ concentration on the hydrogen side, providing a tendency to drive protons toward the steam side—opposite the desired behavior. At open circuit (i.e. zero imposed current), the cell behaves as a concentration cell, driving protons toward the steam side, resulting in a reverse H$_2$ flux. At low current density (near open circuit), the imposed current retards the reverse proton flux. However, at sufficiently low current, the reverse proton flux persists and the faradaic efficiency is small and even negative. As the imposed current increases, the concentration-cell behavior diminishes and the tendency for reverse proton flux is dominated by the desired proton flux to produce H$_2$. Thus, the faradaic efficiency increases as imposed current density increases.

Assuming defect equilibrium at the electrode-electrolyte interfaces and ideal charge-transfer kinetics at the triple-phase-boundary (TPB) regions, Zhu et al [3] reported qualitatively similar characteristics of faradaic efficiency based on the BCZYYb membrane, and also presented very detailed analysis and explanation for the trend of faradaic efficiency.
1.2. Modeling framework

It becomes difficult to compare directly the reported experimental data because materials, temperature, gas-phase partial pressures, gas flow rates, and current-density ranges vary among different studies. Additionally, in no cases are the reported experimental conditions sufficient to unambiguously interpret the results. For example, without knowing gas flow rates and chamber volumes, one cannot determine important gas depletion and dilution that affects faradaic efficiency.

Table 1. Reported protonic-ceramic electrolysis faradaic efficiencies $\eta_f$ with a variety of electrode and electrolyte materials and operating conditions.

| Electrolyte membrane | Steam electrode | $T$ (°C) | $H_2$ collection composition | Flow (sccm) | Steam feed composition | Flow (sccm) | Current (A cm$^{-2}$) | $\eta_f$ (%) | Reference |
|----------------------|----------------|---------|-----------------------------|------------|------------------------|------------|-----------------------|-------------|------------|
| 30 µm                | BLC            | 600     | 0.5 bar H$_2$               | 30         | 80% H$_2$O, 1% O$_2$    | 30         | 0.25                  | 80          | [10]       |
| 10 µm                | BLC            | 600     | 0.5 bar H$_2$               | 30         | 80% H$_2$O, 1% O$_2$    | 30         | 0.25                  | 76          | [14]       |
| 30 µm                | BGCZYYb7111   | 10      | 1.0 1% H$_2$ balance Ar    | 10         | 0% H$_2$O, 4% H$_2$     | 10         | 0.25                  | 100         | [9]        |
| 15 µm                | BGCZYYb4411   | 600     | 5% H$_2$, 3% H$_2$O         | 200        | 3% H$_2$O balance Ar    | 200        | 0.25                  | 91          | [6]        |
| 15 µm                | BGCZYYb4411   | 600     | 5% H$_2$, 3% H$_2$O         | 200        | 3% H$_2$O balance Ar    | 200        | 0.25                  | 97          | [6]        |
| 20 µm                | PNO            | 500     | 0.2 bar H$_2$               | 50         | 0.03 bar H$_2$O         | 50         | 0.25                  | 60          | [11]       |
| 20 µm                | PNO            | 500     | 0.2 bar H$_2$               | 50         | 0.03 bar H$_2$O         | 50         | 0.25                  | 55          | [11]       |

The chemical formulas defining the materials’ abbreviations are as follows:

BCZY27 = BaCe$_0.7$Zr$_{0.3}$Y$_{2}$O$_{3-δ}$, BGLC = Ba$_{1-x}$Ge$_{0.5}$La$_{0.5}$O$_{2-δ}$, BCZYYb7111 = BaCe$_0.7$Zr$_{0.3}$Y$_{2}$O$_{3-δ}$, 
PSCF = PrBa$_{0.5}$Sr$_{0.5}$Co$_{0.5}$Fe$_{0.5}$O$_{3+δ}$, BZY20 = BaZ$_{0.5}$Fe$_{0.5}$O$_{3+δ}$, SFM = Sr$_{2}$Fe$_{1.5}$Mo$_{0.5}$O$_{6-δ}$,

BCZYYb = Ba(Zr$_{0.3}$Ce$_{0.4}$Y$_{2}$O$_{3-δ}$), LSV = (La$_{0.5}$Sr$_{0.5}$)$_{0.5}$O$_{3-δ}$, BCZYYb4411 = BaCe$_0.4$Zr$_{0.6}$Y$_{2}$O$_{3-δ}$, 
PNO = Pr$_2$NiO$_{4+δ}$, (BCZY(45)$_{δ/2}$) = BaCe$_0.36$Zr$_{0.44}$Y$_{2}$O$_{2.9}$, BLC = Ba$_{0.5}$La$_{0.5}$CoO$_{3-δ}$, BCFZY = BaCo$_{0.4}$Fe$_{0.6}$Zr$_{0.2}$Y$_{2}$O$_{3-δ}$

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1.2. Modeling framework

It becomes difficult to compare directly the reported experimental data because materials, temperature, gas-phase partial pressures, gas flow rates, and current-density ranges vary among different studies. Additionally, in no cases are the reported experimental conditions sufficient to unambiguously interpret the results. For example, without knowing gas flow rates and chamber volumes, one cannot determine important gas depletion and dilution that affects faradaic efficiency.
The present paper develops a computational model that predicts electrolysis performance in a laboratory-scale button-cell configuration (figure 2). For the purposes of the present analysis, the gas compositions are fixed on both sides of the membrane-electrode assembly. In other words, the feed gas flows are sufficiently high as to ‘flood’ the cathode and anode sides of the cell. Such flooding is not necessarily the case in all reported experiments.

2. Model formulation and parameter calibration

The underlying model formulation and implementation is documented in numerous prior publications [3–5, 18–24]. Broadly speaking, the model uses a Nernst–Planck representation of charged-defect transport within the electrolyte phase, a Dusty-Gas representation of gas-phase transport within the porous composite electrodes, and a Butler–Volmer representation of the charge-transfer kinetics. Within the electrolyte phase the effective diffusion coefficients of three charged defects (OH\(^{-}\), V\(_{\text{O}}\), and O\(_{\text{O}}\)) are fit to measured conductivities using the Nernst–Einstein relationships. With a focus on the faradaic efficiency, the following paragraphs discuss details of the defect-incorporation chemistry and charge-transfer kinetics.

To be concrete, the model is based upon a thin (15 \(\mu\)m) electrolyte membrane made of BaCe\(_{0.7}\)Zr\(_{0.1}\)Y\(_{0.1}\)Yb\(_{0.1}\)O\(_{3-\delta}\) (BCZYYb) [3]. The anode (steam-side electrode, positrode) is a thin (20 \(\mu\)m) porous triple-conducting oxide made of BaCo\(_{0.4}\)Fe\(_{0.4}\)Zr\(_{0.1}\)Y\(_{0.1}\)O\(_{3-\delta}\) (BCFZY) [25]. The cathode (hydrogen-production side, negatrode) is a thick (500 \(\mu\)m) porous Ni-BCZYYb composite. The models are developed to match published polarization data using the cell in a fuel-cell mode [26]. However, the model is exercised as an electrolysis cell, exploring the effects of operating conditions on faradaic efficiency.
Although equations (2) and (3) offer a global view of the electrolysis chemistry, many more elementary reactions and transport phenomena contribute to the actual performance. Two classes of reactions are relevant. One is charge transfer, transferring charge across phase interfaces (e.g., electrode and electrolyte phases). The other is defect-incorporation, such as Stotz–Wagner hydration that dissociates H$_2$O to produce protons in the electrolyte phase,

$$
\text{H}_2\text{O}(g) + \text{V}^\circ_{\text{O}}(\text{el}) + \text{O}^\circ_2(\text{el}) \rightleftharpoons 2 \text{OH}^\circ_2(\text{el}).
$$

(4)

This is not classified as a charge-transfer reaction because all the charges remain within the electrolyte phase. In any case, electrolysis performance depends on the rates of the contributing reactions. In addition to activities of the participating species, the rates of charge-transfer reactions depend on the electrostatic-potential differences between participating phases.

Defect-incorporation reactions can proceed directly on the surfaces of the proton-conducting electrolyte. Charge-transfer reactions can proceed at triple-phase boundaries (TPBs), at interfaces between the electrode and electrolyte phases, and at the interfaces between the gas and MIEC phase. The present paper uses the Butler–Volmer formulation to represent the charge-transfer reactions at TPB regions.

### 2.1. Negatrode-electrolyte charge-transfer rate

The charge-transfer reaction for the reduction of protons to hydrogen in the negatrode-electrolyte TPB regions (cathode, hydrogen-collection side) can be written globally as

$$
\text{H}_2(g) + 2 \text{O}^\circ_2(\text{el}) \rightleftharpoons 2\text{OH}^\circ_2(\text{el}) + 2e^-(\text{ed}).
$$

(5)

Note that the reaction is written with the forward rate being in the anodic direction (i.e., producing electrons). Using an activation overpotential, $\eta_{\text{act,a}} = E_a - E_a^{\text{eq}}$, the charge-transfer rate can be expressed in a Butler–Volmer format as

$$
\dot{i}_{\text{BV}} = \dot{i}_0 \left[ \exp \left( \frac{\beta_a F \eta_{\text{act,a}}}{RT} \right) - \exp \left( - \frac{\beta_a F \eta_{\text{act,a}}}{RT} \right) \right].
$$

(6)

The exchange current density $\dot{i}_0$ can be expressed as [24]

$$
\dot{i}_0 \equiv \dot{i}_0^* \frac{(p_{\text{H}_2}/p_{\text{H}_2}^*)^{\beta_a/2}}{1 + (p_{\text{H}_2}/p_{\text{H}_2}^*)^{\beta_a/2}} [\text{O}^\circ_2(\text{el})]^{\beta_c} [\text{OH}^\circ_2(\text{el})]^{\beta_a},
$$

(7)

where $\beta_a$ and $\beta_c$ are the anodic and cathodic symmetric factors with $\beta_a + \beta_c = 1$. $p_{\text{H}_2}^*$ and $K_{\text{H}_2}$ are the equilibrium constant of hydrogen adsorption on the metal surface. The temperature dependence of $\dot{i}_0^*$ can be expressed in Arrhenius form as $\dot{i}_0^* = \dot{i}_0^0 \exp(-E/RT)$ with $\dot{i}_0^0$ and $E$ being fitting parameters.

### 2.2. Positrode-electrolyte charge-transfer rate

At the positrode-electrolyte interface (anode, steam-feed side), the overall charge-transfer reaction of water splitting to protons and oxygen can be expressed globally as

$$
2\text{H}_2\text{O}(g) \rightleftharpoons \text{O}_2(g) + 4\text{OH}^\circ_2(\text{el}) + 4e^-(\text{ed}).
$$

(8)

In terms of Butler–Volmer formulation for the charge-transfer rate, the exchange current density can be derived as [24]

$$
\dot{i}_0 = \dot{i}_0^* \frac{(p_{\text{O}_2}/p_{\text{O}_2}^*)^{1/2-\beta_a/4}(p_{\text{H}_2\text{O}}/p_{\text{H}_2\text{O}}^*)^{\beta_a/2}}{1 + (p_{\text{O}_2}/p_{\text{O}_2}^*)^{1/2} + (p_{\text{H}_2\text{O}}/p_{\text{H}_2\text{O}}^*)^{\beta_a/2}} [\text{O}^\circ_2(\text{el})]^{\beta_c} [\text{OH}^\circ_2(\text{el})]^{\beta_a},
$$

(9)

where $\beta_a$ and $\beta_c$ are the anodic and cathodic symmetric factors with $\beta_a + \beta_c = 1$. The parameters $p_{\text{O}_2}^*$ and $p_{\text{H}_2\text{O}}^*$ are the equilibrium constants for O$_2$ and H$_2$O adsorption on the electrode surface. The temperature dependence of $\dot{i}_0^*$ can also be expressed in Arrhenius form.

### 2.3. Defect chemistry

Table 2 lists the incorporation reactions of H$_2$, O$_2$ and H$_2$O on the gas-ceramic interfaces and trapping reaction on the BCZY(Yb) surface and within the membrane bulk [3]. The reactions involve three mobile defects (protons OH$^\circ_2$, oxygen vacancies V$^{\circ\circ}_{\text{O}}$, O-site polarons O$^\circ_2$) and three immobile defects (lattice oxygen O$^\circ_2$, trapped polaron complex (X$^\circ_0$ – O$^\circ_2$)), and untrapped dopants X$^\circ_0$ while X = (Y,Yb). Table 2 lists the
lists the diffusion coefficients for mobile defects. Within the Ni-BCZYYb anode microstructure, the global gas-phase reaction (H$_2$ + 0.5 O$_2$ = H$_2$O) is represented using the detailed heterogeneous reaction mechanism [18].

The defect production rates (mol m$^{-2}$ s$^{-1}$) on the BCZYYb surface can be represented as

$$
\dot{s}_{\text{V}_{\text{O}}^{\bullet}} = -\dot{q}_{\text{O}_2} - \dot{q}_{\text{H}_2}\text{O},
$$

$$
\dot{s}_{\text{OH}_{\text{O}}^{\bullet}} = 2\dot{q}_{\text{H}_2}\text{O} + \dot{q}_{\text{H}_2},
$$

$$
\dot{s}_{\text{O}_{\text{O}}^{\bullet}} = 2\dot{q}_{\text{O}_2} - \dot{q}_{\text{H}_2} - \dot{q}_{\text{Trap}},
$$

$$
\dot{s}_{(X_{\text{A}} - \text{O}_{\text{O}}^{\bullet})} = \dot{q}_{\text{Trap}},
$$

where the reaction rates of progress are evaluated as

$$
\dot{q}_{\text{H}_2} = k_{\text{f},\text{H}_2}[\text{H}_2]^{1/2}[\text{O}_{\text{O}}^{\bullet}] - k_{\text{b},\text{H}_2}[\text{OH}_{\text{O}}^{\bullet}],
$$

$$
\dot{q}_{\text{O}_2} = k_{\text{f},\text{O}_2}[\text{O}_2]^{1/2}[\text{V}_{\text{O}}^{\bullet}] - k_{\text{b},\text{O}_2}[\text{O}_{\text{O}}^{\bullet}]^{12},
$$

$$
\dot{q}_{\text{H}_2}\text{O} = k_{\text{f},\text{H}_2}\text{O}[\text{H}_2\text{O}]^{1/2}[\text{V}_{\text{O}}^{\bullet}]^{12} - k_{\text{b},\text{H}_2}\text{O}[\text{OH}_{\text{O}}^{\bullet}]^{12},
$$

$$
\dot{q}_{\text{Trap}} = k_{\text{f},\text{Trap}}[X_{\text{A}}]^{12}[\text{O}_{\text{O}}^{\bullet}] - k_{\text{b},\text{Trap}}[(X_{\text{A}}^{\bullet} - \text{O}_{\text{O}}^{\bullet})].
$$

The forward and backward rate expressions are denoted as $k_{ij}$ and $k_{ji}$, which are related to the equilibrium constants as $K_{ij} = k_{ij}/k_{ji}$. In other words, the reactions are microscopically reversible.

Fitted net enthalpy and entropy changes for each reaction. Table 3 lists the diffusion coefficients for mobile defects. Within the Ni-BCZYYb anode microstructure, the global gas-phase reaction (H$_2$ + 0.5 O$_2$ = H$_2$O) is represented using the detailed heterogeneous reaction mechanism [18].

The defect production rates (mol m$^{-2}$ s$^{-1}$) on the BCZYYb surface can be represented as

| Reactions | $\Delta H^\circ$ (kJ mol$^{-1}$) | $\Delta S^\circ$ (J mol$^{-1}$ K$^{-1}$) | $K_p$ (600 °C) |
|-----------|--------------------------------|----------------------------------|----------------|
| $\frac{1}{2}$H$_2$ + O$_{\text{O}}^{\bullet}$ = OH$_{\text{O}}^{\bullet}$ | $-252.37$ | $-54.33$ | $1.82 \times 10^{12}$ |
| $\frac{1}{2}$O$_2$ + O$_{\text{O}}^{\bullet}$ + V$_{\text{O}}^{\bullet}$ = 2O$_{\text{O}}^{\bullet}$ | $+114.88$ | $-60.30$ | $9.49 \times 10^{-11}$ |
| H$_2$O + V$_{\text{O}}^{\bullet}$ + O$_{\text{O}}^{\bullet}$ = 2OH$_{\text{O}}^{\bullet}$ | $-130.00$ | $-126.47$ | $1.48 \times 10^{-4}$ |
| X$_{\text{A}}$ + O$_{\text{O}}^{\bullet}$ = (X$_{\text{A}}$ - O$_{\text{O}}^{\bullet}$) | $-90.00$ | $-14.41$ | $4.28 \times 10^{-4}$ |
| H$_2$ + $\frac{1}{2}$O$_2$ = H$_2$O | $-248.11$ | $-55.48$ | $8.81 \times 10^{-11}$ |

| Reactions | $D^\circ$ (m$^2$ s$^{-1}$) | $E_k$ (kJ mol$^{-1}$) | $D_k$ (500 °C) (m$^2$ s$^{-1}$) | $D_k$ (700 °C) (m$^2$ s$^{-1}$) |
|-----------|----------------|----------------|----------------|----------------|
| OH$_{\text{O}}^{\bullet}$ | $1.02 \times 10^{-10}$ | $42.65$ | $1.35 \times 10^{-10}$ | $5.26 \times 10^{-10}$ |
| V$_{\text{O}}^{\bullet}$ | $1.73 \times 10^{-10}$ | $59.70$ | $1.60 \times 10^{-11}$ | $1.08 \times 10^{-10}$ |
| O$_{\text{O}}^{\bullet}$ | $2.41 \times 10^{-10}$ | $8.40$ | $6.51 \times 10^{-10}$ | $8.52 \times 10^{-10}$ |

Table 2. Thermodynamics of defect reactions for BCZYYb [3].

Table 3. Diffusion coefficients of mobile defects for BCZYYb [3].
Table 4. Selected equilibrium lattice-scale defect concentrations in BCZYYb at 600 °C and atmospheric pressure.

|                  | 97% H₂, 3% H₂O   | 80% O₂, 20% H₂O |
|------------------|-------------------|-----------------|
| [OH⁴⁻]⁺         | 1.5945 × 10⁻¹⁰    | 1.8379 × 10⁻¹⁰  |
| [O²⁻]⁺          | 2.0275 × 10⁻¹²    | 4.0639 × 10⁻¹³  |
| [O³⁻]⁻          | 4.4123 × 10⁻¹⁰    | 9.8406 × 10⁻⁰⁷  |
| [O⁵⁻]⁻          | 2.8203 × 10⁻⁰⁰    | 2.8041 × 10⁻⁰⁰  |
| [(X⁶⁺ − O⁷⁻)]²⁻ | 3.7759 × 10⁻⁰⁹    | 8.0811 × 10⁻⁰³  |

Despite the typical equilibrium assumption, there is evidence for defect-incorporation rate limitations (cf [22]). The present study considers the potential effects of defect-incorporation kinetics on the faradaic efficiency. Unfortunately, there are no available experimental data with which to evaluate the defect incorporation rates. Thus, somewhat arbitrarily for the purposes of estimating possible effects, the same rate coefficient $k_f$ is used to express the forward rate for all the defect-incorporation reactions (i.e. $k_{f_H₂}$, $k_{f_H₂O}$, $k_{f_{O₂}}$, and $k_{f_{Trap}}$) at the gas-BCZYYb interfaces. It should be noted that the value of $k_f$ considers both the actual defect reaction rates and the effective BCZYYb surface exposed to the gas-phase environment. Additionally, each $k_{f,i}$ may have very different units for each defect reaction. In any case, because the reactions are microscopically reversible, as $k_f$ becomes sufficiently large, the steady-state defect concentrations resulting from the defect-incorporation reactions alone will asymptotically reach the equilibrium state. Experiments such as conductivity-relaxation measurements could provide needed kinetics for the defect incorporation rates.

2.4. Reduced cerium polaron

In materials such as BCZYYb under extremely highly reducing conditions, it might be possible to form a reduced-cerium polaron Ce₃⁺. In materials such as gadolinium-doped ceria, reduced-cerium polarons surely introduce n-type conductivity under reducing conditions [29, 30]. If this would occur in BCZYYb, some n-type electronic conductivity would likely affect the faradaic efficiency. However, based on single-atmosphere BCZYYb conductivity measurements in moist reducing conditions (figure 3), there is no evidence of n-type conductivity [3]. The present BCZYYb models are consistent with these data [3]. Moreover, because the hydrogen-collection side remains moist, the gas-phase H₂O dissociation should produce sufficient oxygen so as to avoid extremely reducing conditions. Consequently, the present electrolysis models neglect the possibility that reduced-cerium polarons could be present. Nevertheless, there is some possibly contradictory evidence. Studying BZY and BCZY with 10% of cerium (BCZY18), Dippon et al [31] reported no significant electronic leakage. However, they reported that increasing the cerium content to 20% (BCZY27) was sufficient to observe electronic leakage. In principle, models could be extended to include the possible effects of reduced-cerium small polarons. However, doing so would require new experimental data from which to determine needed thermodynamic and transport parameters.

2.5. Model tuning and validation

As in most models, there are numerous parameters that cannot be measured directly and thus demand some empiricism. The present model is calibrated against recently published data from a button cell operating under fuel-cell polarization [26]. Figure 4 illustrates the comparison between measured and modeled polarization. Table 5 lists relevant parameters that are used in the present model.
Figure 4. Comparison of measured and modeled atmospheric fuel-cell button-cell voltage and power density as functions of current density [26]. The gas-phase compositions are moist H\textsubscript{2} on the negatrode (anode) side and moist air on the positrode (cathode) side.

Table 5. Parameters for modeling the MEA structure.

| Parameters                          | Value   | Units   |
|-------------------------------------|---------|---------|
| Negatrode (fuel-cell anode, electrolysis cathode) |         |         |
| Thickness ($L_a$)                   | 500     | µm      |
| Porosity ($\phi_g$)                 | 0.35    |         |
| Ni volume fraction ($\phi_{Ni}$)    | 0.35    |         |
| BCZYYb volume fraction ($\phi_{BCZYYb}$) | 0.30    |         |
| Tortuosity ($\tau_g$)               | 4.50    |         |
| Ni particle radius ($r_{Ni}$)       | 0.50    | µm      |
| BCZYYb particle radius ($r_{BCZYYb}$) | 0.50    |         |
| Specific catalyst area ($A_s$)      | $5.0 \times 10^3$ | cm\textsuperscript{-1} |
| Exchange current factor ($i_0$)     | $1.72 \times 10^6$ | A cm\textsuperscript{-1} |
| Exchange current activation energy ($E$) | 82.60  | kJ mol\textsuperscript{-1} |
| Anodic symmetry factor ($\alpha_a$)  | 0.30    |         |
| Cathodic symmetry factor ($\alpha_c$) | 0.70    |         |
| Positrode (fuel-cell cathode, electrolysis anode) |         |         |
| Thickness ($L_c$)                   | 20      | µm      |
| Porosity ($\phi_g$)                 | 0.35    |         |
| BCFZY volume fraction ($\phi_{BCFZY}$) | 0.65    |         |
| Tortuosity ($\tau_g$)               | 4.50    |         |
| BCFZY particle radius ($r_{BCFZY}$)  | 0.50    | µm      |
| Exchange current factor ($i_0$)     | $2.48 \times 10^5$ | A cm\textsuperscript{-1} |
| Exchange current activation energy ($E$) | 43.36  | kJ mol\textsuperscript{-1} |
| Anodic symmetry factor ($\alpha_a$)  | 0.80    |         |
| Cathodic symmetry factor ($\alpha_c$) | 0.20    |         |
| Dense electrolyte membrane          |         |         |
| Thickness ($L_{el}$)                | 15      | µm      |

3. Predicted faradaic efficiencies

The button-cell model is used to predict faradaic efficiencies for wide ranges of operating conditions.

3.1. Temperature effects

Figure 5 shows predicted cell voltage, power density, and faradaic efficiency as functions of the current density at four operating temperatures (500 °C, 600 °C, 700 °C, and 800 °C). The gas-phase compositions are 97% H\textsubscript{2} and 3% H\textsubscript{2}O within the hydrogen-collection chamber (negatrode side) and 80% O\textsubscript{2} and 20% H\textsubscript{2}O within the steam-feed chamber (positrode side). The gas-phase pressures in both chambers are
maintained to be atmospheric. As the operating temperature increases, figure 5 shows that the faradaic efficiencies decrease greatly, demanding much less voltage and power to operate the cell.

As the temperature increases, the equilibrium proton concentration $[\text{OH}^\bullet\text{O}]$ and transference number decrease while the concentrations and transference number of $\text{V}^{\bullet\bullet}\text{O}$ and $\text{O}^\bullet\text{O}$ increase, both contributing to much lower faradaic efficiency. At higher temperatures the charge-transfer rates and the electrolyte membrane conductivity increase, serving to reduce the activation and ohmic polarization losses. Thus, significantly lower voltage and power are required to achieve the same defect fluxes though the cell.

3.2. Pressure effects
Figure 6 illustrates the effects of gas-phase pressure on faradaic efficiency. The cell is operating at a fixed temperature of $T = 600 \, ^\circ\text{C}$, but with pressures ranging as $1 \leq p \leq 30$ atm. The gas-phase compositions are 97% $\text{H}_2$ and 3% $\text{H}_2\text{O}$ within the hydrogen-collection chamber and 80% $\text{O}_2$ and 20% $\text{H}_2\text{O}$ within the steam-feed chamber. Increasing pressure serves to increase faradaic efficiency. However, increased pressure requires slightly higher cell voltage and electric power. Compared to the effects of temperature, the effects of operating pressure are much weaker.

3.3. $\text{H}_2\text{O}-\text{O}_2$ composition
In practical electrolysis technology (e.g. planar or tubular configurations), depending on flow rates, the feed steam can be significantly diluted with the $\text{O}_2$ product. Such dilution can significantly affect the faradaic efficiency. Figure 7 illustrates the effects of the gas-phase composition within the steam-feed chamber. In this case, the cell temperature and pressure are fixed as $T = 600 \, ^\circ\text{C}$ and $p = 1.0$ atm. The composition of the hydrogen–collection chamber is fixed as 97% $\text{H}_2$ and 3% $\text{H}_2\text{O}$. The steam-side oxygen concentration varies between 1% and 80%, with the balance being $\text{H}_2\text{O}$.

As the $\text{O}_2$ concentration increases, the small-polaron concentration ($[\text{O}_2^\bullet]$) at the positrode-electrolyte interface increases, thus increasing the $\text{O}_2^\bullet$ concentration gradient through the electrolyte membrane and increasing electronic current via $\text{O}_2^\bullet$ flux. This electronic leakage reduces faradaic efficiency. Figure 7 shows lower faradaic efficiency as the $p_{\text{O}_2}$ increases. Figure 7 also shows that as $\text{O}_2$ concentration increases more power is required to maintain a certain current density.
Figure 6. Predicted cell voltage, power density, and faradaic efficiency as functions of imposed current density at four operating pressures.

Figure 7. Predicted cell voltage, power density, and faradaic efficiency as functions of imposed current density. The gas-phase composition in the hydrogen-collection chamber is fixed at 97% H$_2$ and 3% H$_2$O. Within the steam chamber, the O$_2$ concentration varies, with the balance being H$_2$O. The gas-phase pressures are fixed at $p = 1$ atm.
3.4. Defect incorporation rates

Figure 8 shows fluxes of three mobile defects \( \text{OH}\,^* \), \( \text{V}_\text{O}^{**} \) and \( \text{O}^\bullet_\text{O} \) through the dense BCZYYb electrolyte membrane and the faradaic efficiency as functions of the defect-incorporation rate \( k_i \) at the BCZYYb surfaces. The gas composition is fixed as 97% \( \text{H}_2 \) and 3% \( \text{H}_2\text{O} \) in the hydrogen compartment and 80% \( \text{O}_2 \) and 20% \( \text{H}_2\text{O} \) in the steam compartment. The pressure is \( p = 1 \text{ atm} \) and the temperature is \( T = 600 \text{ °C} \). The imposed current density is fixed at \( i = 0.5 \text{ A cm}^{-2} \). At the very low defect-incorporation rate of \( k_i = 1.0 \), figure 8 shows that the proton flux \( j_{\text{OH}^\bullet} \) through the electrolyte membrane dominates and the polaron flux \( j_{\text{V}_\text{O}^{**}} \) and oxygen vacancy flux \( j_{\text{O}^\bullet_\text{O}} \) are negligibly small. Thus the faradaic efficiency for \( k_i = 1.0 \) is about 99.8% and the electrolyte membrane behaves essentially as a pure proton-conducting membrane. As \( k_i \) increases, the proton flux \( j_{\text{OH}^\bullet} \) decreases, but the polaron flux \( j_{\text{V}_\text{O}^{**}} \) and oxygen vacancy flux \( j_{\text{O}^\bullet_\text{O}} \) increases. Thus, the faradaic efficiency decreases. At the highest rate \( k_i = 10^6 \), the faradaic efficiency drops to about 76.6%.

As indicated in equations (5) and (8), the charge-transfer reaction at the posttode-electrolyte interface in the electrolysis mode acts to split \( \text{H}_2\text{O} \) to produce \( \text{OH}^\bullet \) into the electrolyte, while the charge-transfer reaction at the negatode-electrolyte interface (i.e. equation (5)) consumes \( \text{OH}^\bullet \) from the electrolyte to produce \( \text{H}_2 \) into the negatode. Thus, the current charge-transfer models only involve the \( \text{OH}^\bullet \) entering (producing) or leaving (consuming) the electrolyte membrane (at the electrode-electrolyte interfaces), and \( \text{V}_\text{O}^{**} \) and \( \text{O}^\bullet_\text{O} \) can only be produced on the surface of the BCZYYb electrolyte membrane exposed to the gas environment through the defect reactions. As long as the surface area of the dense electrolyte membrane is small or the defect reaction rate is small (i.e. low value of \( k_i \) ), the transport of \( \text{V}_\text{O}^{**} \) and \( \text{O}^\bullet_\text{O} \) through the electrolyte membrane is blocked at the electrode-electrolyte interfaces, leading to almost pure proton conduction through the electrolyte membrane, and therefore, high faradaic efficiency of the cell.

On the BCZYYb electrolyte membrane surface exposed to \( \text{O}_2\text{-H}_2\text{O} \) environment (posttode side), the \( \text{O}_2 \) incorporation reaction (\( \frac{1}{2}\text{O}_2 + \text{O}^\bullet_\text{O} + \text{V}_\text{O}^{**} = 2\text{O}^\bullet_\text{O} \)) produces \( \text{O}^\bullet_\text{O} \) into the BCZYYb electrolyte membrane. The \( \text{H}_2 \) incorporation reaction (\( \frac{1}{2}\text{H}_2 + \text{O}^\bullet_\text{O} = \text{OH}^\bullet \)) and \( \text{H}_2\text{O} \) incorporation reaction (\( \text{H}_2\text{O} + \text{V}_\text{O}^{**} + \text{O}^\bullet_\text{O} = 2\text{OH}^\bullet \)) consume \( \text{OH}^\bullet \) within the electrolyte to produce \( \text{H}_2 \) and \( \text{H}_2\text{O} \) into the gas environment within the posttode. It should be noted that the net rate of \( H_2 \) incorporation is small compared to the \( \text{O}_2 \) and \( \text{H}_2\text{O} \) incorporation rates as \( k_i \) increases. Figure 9 shows that the defect-incorporation reactions lead to decreasing [\( \text{OH}^\bullet \)] and increasing [\( \text{O}^\bullet_\text{O} \)] and [\( \text{V}_\text{O}^{**} \)] on the posttode side.

On the BCZYYb electrolyte membrane surface exposed to \( \text{H}_2\text{-H}_2\text{O} \) environment (hydrogen collection, negatode side), the \( \text{O}_2 \) incorporation reaction is reversed to consume \( \text{O}^\bullet_\text{O} \) in the BCZYYb electrolyte membrane to produce \( \text{O}_2\text{(g)} \) into the negatode pore volume. The \( \text{H}_2 \) reacts with \( \text{O}^\bullet_\text{O} \) to produce \( \text{OH}^\bullet \), and the \( \text{H}_2\text{O} \) incorporation reaction is reversed to produce \( \text{H}_2\text{O} \). The \( \text{O}_2 \) produced from reversing the \( \text{O}_2 \) incorporation reaction can react with \( \text{H}_2 \) to make \( \text{H}_2\text{O} \) on the Ni surface within the negatode microstructure. Figure 9 shows that [\( \text{O}^\bullet_\text{O} \)] decreases as \( k_i \) increases, but [\( \text{OH}^\bullet \)] and [\( \text{V}_\text{O}^{**} \)] do not vary monotonically because of competition among the defect-incorporation reactions. As illustrated in figure 9, it is clear that [\( \text{O}^\bullet_\text{O} \)] increases at the steam side, but decreases at the hydrogen side as \( k_i \) increases. Thus the [\( \text{O}^\bullet_\text{O} \)] gradient across the BCZYYb membrane increases, leading to increasing \( \text{O}^\bullet_\text{O} \) flux \( j_{\text{O}^\bullet_\text{O}} \), but lower proton flux \( j_{\text{OH}^\bullet} \), decreasing faradaic efficiency as illustrated in figure 8.
Figure 9. Defect concentrations in the BCZYYb electrolyte membrane at the posttode-electrolyte and negatode-electrolyte interfaces as functions of defect-incorporation rates. The imposed current density is fixed at $i = 0.5 \text{ A cm}^{-2}$.

Figure 10. Predicted cell voltage, power density, and faradaic efficiency as functions of current density. The defect-incorporation forward rate constant is specified as $k_f = 10^0, 10^1, 10^2, 10^3, 10^4, 10^5, 10^6$. The gas-phase composition is 97% H$_2$ and 3% H$_2$O on the hydrogen-collection side and 80% O$_2$ and 20% H$_2$O on the steam-feed side. The operating temperature is fixed at 600 $^\circ$C and the pressure is atmospheric.

Figure 10 shows faradaic efficiency as a function of current density with fixed defect-incorporation reaction rates on the BCZYYb surfaces. As the current density increases in electrolysis mode, the proton fluxes from the charge-transfer processes increase while the defect reaction rates on the BCZYYb surface are fixed. Thus, the faradaic efficiency increases as the current density increases. Figure 10 also compares the faradaic efficiency with defect-incorporation forward rates specified as $k_f = 10^0, 10^1, 10^2, 10^3, 10^4, 10^5, 10^6$. Consistent with figure 8, the faradaic efficiency decreases as $k_f$ increases at the same current density.

Figure 10 shows that the cell voltage and power drop slightly at the same current density as $k_f$ increases. Since the small polaron O$_{\bullet}$ has higher mobility than that of the proton OH$_{\bullet}$, the higher O$_{\bullet}$ flux at higher $k_f$
leads generally to higher electronic conductivity through the BCZYYb membrane, and hence lower cell voltage.

3.5. Energy efficiency

Faradaic efficiency is certainly a valuable measure of electrolysis performance. But it is not the only useful measure. The energy efficiency is a more useful measure of economic effectiveness. Energy efficiency is evaluated as

\[
\eta_E = \frac{J_{H_2} \Delta H_{H_2}}{i_{cell}} = \frac{\Delta H_{H_2}}{2FE_{cell}} = \frac{E_0^\circ}{E_{cell}} \eta_F, \tag{19}
\]

where \(\Delta H_{H_2}\) is the lower heating value of the produced \(H_2\) and \(E_0^\circ\) is the thermal-neutral voltage. As equation (19) shows, the faradaic efficiency and energy efficiency are related through the thermal-neutral voltage. In practice the energy efficiency provides a measure of the electricity cost compared to the value of the produced hydrogen.

Especially at low temperature the energy efficiency is qualitatively different from the faradaic efficiency (figure 11). Figures 5–10 show the cell voltage \(E_{cell}\) required to maintain a certain current density depends on operating conditions. Equation (19) shows how the cell voltage affects the relationship between energy efficiency and faradaic efficiency.

3.6. Effects of the electrolyte membrane thickness

Figure 12 illustrates the predicted effects of electrolyte membrane thickness on the operating cell voltage, faradaic efficiency, and energy efficiency. The gas compositions are fixed at 97% \(H_2\) and 3% \(H_2O\) in the hydrogen compartment and 80% \(O_2\) and 20% \(H_2O\) in the steam compartment. The gas-phase pressure is atmospheric and the temperature is 600 °C. Two electrolyte membrane thicknesses are considered: \(L_{el} = 15 \, \mu m\) and \(L_{el} = 30 \, \mu m\).

Figure 12(a) shows that the operating cell potentials for \(L_{el} = 30 \, \mu m\) are substantially greater than those for \(L_{el} = 15 \, \mu m\), especially at high current density. Increasing the electrolyte membrane thickness affects the defect concentration profiles and transport through the membrane, thus affecting the ohmic polarization and also the charge-transfer rates at the electrode-electrolyte interfaces.

Figure 12(b) also shows that increasing the membrane thickness tends to increase the faradaic efficiency, particularly at low current density. At high current density the faradaic efficiency improvement is small. As illustrated in figure 12(c), the energy efficiency is qualitatively different from the faradaic efficiency. At low current density, the energy efficiency is higher for the thicker membrane. At higher current density, the thinner membrane has higher energy efficiency.
Figure 12. Comparison of cell voltage, faradaic and energy efficiencies as functions of current density at two electrolyte membrane thicknesses: $L_{el} = 15 \mu m$ and $L_{el} = 30 \mu m$.

4. Current-density dependencies

Based on the definition of faradaic efficiency and the electrochemical properties of mixed-conducting electrolytes, the functional form of the faradaic efficiency, especially at low current density, must behave qualitatively as illustrated in figure 1. That is, faradaic efficiency increases as electrolysis current density increases. Nevertheless, there are published experimental observations that show the opposite [8–12].

Vøllestad et al [10] discuss the possibility that high overpotentials may tend to reduce faradaic efficiency at high current density. The present model assumes that gas-phase partial pressures represent the activities in the evaluation of reaction rates in mass-action kinetics. If, however, as Vøllestad et al suggest, high overpotentials increased the effective activity of O$_2$, then the incorporation rate of O-site polarons would be greater than that predicted if the O$_2$ activity were based on gas-phase oxygen partial pressure alone, leading to increased leakage current and decreased faradaic efficiency. Such behavior would depend on the electrocatalytic behavior of the postrode, with different postrode compositions leading to different observed faradaic efficiencies. Vøllestad et al call particular attention to the oxidation of Co in their Ba$_{1-x}$Gd$_{0.4}$La$_{0.2}CoO$_{6-δ}$ postrode. Duan et al [7] reported that higher pO$_2$ and lower pH$_2$O at postrode-electrolyte interfaces serve to decrease faradaic efficiency. If the effective O$_2$ activity were higher than its partial pressure, the decreasing faradaic efficiency would be consistent with the trend shown in figure 13.

The present model suggests that observed faradaic efficiencies could be caused by unmeasured variations in cell operating conditions as functions of current density. Figure 13 shows the possible effects of temperature (figure 5) and steam-side dilution (figure 7) on predicted faradaic efficiency. The overlaid red arrows indicate the possibility that as temperature increases or steam dilution increases, faradaic efficiency decreases. As current density increases, the ohmic heating within the electrolysis cell certainly increases, tending to raise temperature. Similarly, as current density increases, the tendency to increase steam-side dilution with O$_2$ increases. There are essentially no published papers that report sufficient information about experimental conditions to determine the extent of cell-temperature of steam-dilution variations. Thus, it is certainly plausible that reports of faradaic efficiency decreasing as a function of increasing imposed current are the result of unobserved operating conditions changing. To confirm, or refute, this behavior, the actual cell temperature (not the furnace temperature) must be measured. Similarly, the gas-phase compositions must be measured at the interfaces with the cell.
5. Summary and conclusions

This paper develops and exercises a physics-based model to characterize the behavior of electrolysis-cell faradaic efficiency as functions of temperature, pressure, gas compositions, etc. To be concrete, the model is based upon a Ni-BCZYYb | BCZYYb | BCFZY membrane-electrode structure. The model assumes that the electronic flux through the membrane is in the form of a positively charged small polaron. The model is developed and calibrated using measured material properties and polarization behavior.

The faradaic efficiency has a characteristic shape as a function of applied current density. Near open circuit, the faradaic efficiency is low, even negative. As the imposed current density increases the faradaic efficiency also increases. Although the qualitative behavior remains, the quantitative behavior of the faradaic efficiency depends on temperature, pressure, and gas-phase compositions.

Although the model predicts and interprets the behavior of faradaic efficiency, there is conflicting literature on the functional behavior. Even for the same, or very similar materials, some researchers report that faradaic efficiency increases as imposed current density increases [3–7]. This is consistent with the present model. However, other papers report just the opposite behavior. That is, the faradaic efficiency is high near open circuit and decreases as imposed current density increases [8–12]. For the same materials and operating conditions, these opposite behaviors cannot both be correct.

The model suggests a possible explanation for the apparently contradictory behavior of measured faradaic efficiency. As imposed current density increases, the ohmic heating within the membrane and charge-transfer polarizations at the electrode-electrolyte interfaces increase, tending to increase the cell temperature. As temperature increases, faradaic efficiency decreases (cf figures 5 and 13). If the cell temperature was not directly measured it could be significantly higher than the furnace setpoint temperature. If this was the case and the cell temperature was assumed to be the furnace temperature, the faradaic efficiency would appear to decrease as current density increased. Similar misinterpretations could occur if the gas-phase compositions were changing as functions of current density. If gas feed flow rates were small, composition variations would be possible. No published papers provide sufficient experimental and operational details from which these possible behaviors can be quantitatively assessed. Thus, although the model-based interpretations are reasonable, they cannot be independently confirmed.

The present model neglects the possibility that n-type electronic conductivity can be induced in the form of reduced-cerium polarons under extremely reducing conditions. Based on measured conductivity for BCZYYb, there is no evidence to suggest any n-type conductivity even at oxygen pressures as low as $p_{O_2} = 10^{-25}$ atm (cf figure 3). However, Dippon et al [31] find that cerium content in BCZY materials can introduce electronic conductivity. Thus, the possibility of reduced-cerium polarons remains an open issue, with potentially significant impact on faradaic efficiency.

Inasmuch as faradaic efficiency is a practically useful and widely reported measure of electrolysis performance, its qualitative and quantitative interpretation is important. For a particular electrolysis cell using the same materials, cell architecture, and operating conditions, the behavior of the faradaic efficiency

![Figure 13. Possible effects on faradaic efficiency if operating conditions depend on current density.](image)
must be unique. The present model provides quantitative insight that assists translation of faradaic efficiency.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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