Supplementary Information (SI) for Energy & Environmental Science.

Electronic Supplementary Information

Water electrolysis technologies: the importance of new cell designs and fundamental modelling to guide industrial-scale development

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1. Equations for fluid flow

The Navier-Stokes (N-S) equations (S1-S2) are used for momentum and mass conservation in the fluid flow:[1]

$$\rho \frac{\partial \vec{u}}{\partial t} + \rho(\vec{u}.\nabla)\vec{u} = \nabla.\{-P\vec{I} + \mu[\nabla\vec{u} + (\nabla\vec{u})^{T}]\} + F_{ST} + \rho g \tag{S1}$$

$$\nabla.\vec{u} = 0 \tag{S2}$$

where $\vec{u}$ is the velocity field ($m \cdot s^{-1}$), P is pressure (Pa), g is the force of gravity ($m \cdot s^{-2}$), ρ is the density ($kg \cdot m^{-3}$), μ is the dynamic viscosity ($Ns \cdot m^{-2}$), T is the absolute temperature (K), F_{ST} is the source term of the interfacial tension at the interface and $\vec{I}$ is the identity matrix.

2. Equations for electrolyser cell voltage

Overall, the cell voltage V_{cell} of an electrolyser is composed of several components:[2, 3]

$$V_{cell} = V_{ocv} + V_{act} + V_{ohm} + V_{diff} \tag{S3}$$

where V_{ocv} is the open-circuit voltage (V), V_{act} is the activation overvoltage (V), V_{ohm} is the ohmic overvoltage (V), and V_{diff} is the diffusion overvoltage (V).

The open-circuit voltage V_{ocv} for water electrolysis can be derived from the Nernst equation as follows:

$$V_{ocv} = V^{0}_{std} + (T - T_{ref})\frac{\Delta S^{0}}{nF} + \frac{RT}{2F}\left[ln\left(\frac{P_{H_2}\sqrt{P_{O_2}}}{\alpha_{H_2O,\ elec}}\right)\right] \tag{S4}$$

where V_{std}^{0} is the standard reversible cell voltage, which is 1.229 V at 25 °C and 1 atm, P_{H_2} is the effective partial pressure of hydrogen at the cathode, $P_{O_2}$is the effective partial pressure of oxygen at the anode, F is the Faraday constant (96,500 C·mol^{-1}), R is the universal gas constant (8.3143 J·mol^{-1}·K^{-1}), T is the temperature (K), and n is the number of electrons involved. The second term in the equation accounts for any change in reversible potential at temperatures that are different from the reference standard temperature, where $\frac{\Delta S^0}{nF}$ is the standard entropy change (–0.9 x 10^{-3} J·mol^{-1}·K^{-1}), and $\alpha_{H_2O,\ elec}$ is the water activity of the electrolyte solution.

V_{act} is related to the kinetics of charge transfer reactions that occur on the electrode surface. Bubble coverage by produced gases renders some of the electrode surface inactive, which can be included in V_{act} by re-scaling the free surface area of electrode contributing to the current density during gas-evolving electrolysis reactions:

$$V_{act} = \frac{RT}{\alpha_{an}F} ln\left[\frac{i}{i_0^{an}(1-\theta_{an})}\right] + \frac{RT}{\alpha_{cat}F} ln\left[\frac{i}{i_0^{cat}(1-\theta_{cat})}\right] \tag{S5}$$

Where i is the current density (A·m^{-2}); α_{an} and α_{cat} are charge transfer coefficients of the anode and cathode, respectively; θ represents the bubble coverage over the electrodes (θ_{an} for the anode and θ_{cat} for the cathode), which can be determined by several empirical relations; i_0^{an} and i_0^{cat} are the effective exchange current densities of the anode and cathode, respectively.

V_{ohm} is caused by the resistance of different components of an electrolyser with most resistance coming from the electrolyte, and the other two main contributions come from electrode and separator. This overpotential is directly proportional to the current I flowing through the cell as per Ohm's law:

$$V_{ohm} = I\left(R_e + R_{el} + R_s\right) \tag{S6}$$

where R_e is the total electrode resistance (Ω) of anode and cathode, R_{el} is the electrolyte resistance, and R_s is the separator resistance. The resistance of each component is dependent on the properties of its material and its geometry via:

$$R = \rho\left(\frac{l}{A}\right) \tag{S7}$$

where the current flows in a path of length l with cross-sectional area A in a material with resistivity ρ.

$$R_e = \left[\frac{\rho_o^{j}\,\delta_j}{A_e(1-\varepsilon)^{3/2}}\right] \cdot \left[1 + k_j(T - T_{ref})\right] \tag{S8}$$

$$R_{el} = \left[\frac{\rho_{el}(l_{j-s} - \beta_j)}{A_e}\right] + \left[\frac{\rho_{el}\,\beta_j}{A_e(1-\theta_j)^{3/2}}\right] \tag{S9}$$

$$R_s = = \frac{\rho_{el}\,\delta_s\,\tau^2}{w_s\,\varepsilon_s\,A_s} \tag{S10}$$

where j is the electrode (either anode or cathode), δ_j and δ_s are the electrode and separator thicknesses respectively (cm) , A_e and A_s are the areas of electrode and separator respectively (cm^2), ε is the electrode porosity, l_{j-s} is the width of electrolyte zone (cm), β is the thickness of the bubble zone (cm) in the electrolyte, θ is the void fraction, τ is the tortuosity, ρ_o and ρ_{el} are the resistivity of electrode and electrolyte without bubbles (Ω·cm), k is the temperature coefficient of the resistivity (K^{-1}), and w_s is the wettability factor of the separator for the electrolyte.

At higher current densities, reaction is no longer controlled by electron transfer only and the diffusion of species also matters, causing an additional overpotential, known as diffusion or mass transport overpotential, V_{diff}. This arises due to the gradient in the reactant concentration in the vicinity of the electrode surface and is modelled by combining the Nernst equation with Fick's law of diffusion:

$$V_{diff} = \frac{RT}{4F} ln\left(\frac{C_{O_{2,el}}^{an}}{C_{O_{2,o}}^{an}}\right) + \frac{RT}{2F} ln\left(\frac{C_{H_{2,el}}^{cat}}{C_{H_{2,o}}^{cat}}\right) \tag{S11}$$

where ($C_{H_{2,el}}^{cat}$, $C_{O_{2,el}}^{an}$) represent the molar concentrations (mM) of hydrogen and oxygen at the interface of electrode and electrolyte and ($C_{O_{2,o}}^{an}$,$C_{H_{2,o}}^{cat}$) represent the molar concentrations (mM) of oxygen and hydrogen at the anode and cathode respectively, under reference working conditions.

References

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