

Flexible Dispatch Strategy of Electric Grid Integrating PEM Electrolyzer for Hydrogen Generation

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Supplementary Material

0D electrochemical model of the PEM electrolyser

Under irreversible condition, the operating voltage of an electrolyzer cell (V_{op} , in V) is estimated by the voltage under reversible condition (V_{rev} , in V) plus three types of overvoltages [1, 2]:

$$V_{op} = V_{rev} + V_{ohm} + V_{conc} + V_{act} \quad (S.1)$$

where V_{ohm} , V_{conc} , V_{act} (in V) are the ohmic, concentration and activation overvoltages, respectively.

The reversible voltage can be determined by applying the pressure correction based on Nernst equation [3]:

$$V_{rev} = V_{rev,0} + \frac{R \cdot T}{2 \cdot F} \ln \left(\frac{(p_{cat} - p_{H_2O}) \cdot (p_{an} - p_{H_2O})^{0.5}}{p_{H_2O}} \right) \quad (S.2)$$

where R is the gas constant (equal to 8.314 J/(mol·K)), F is the Faraday constant (equal to 96,485 C/mol), T (in K) is the operating temperature, p_{cat} and p_{an} (in bar) are pressure in cathodic and anodic compartment, p_{H_2O} (in bar) is the water vapor pressure which is calculated according to an empirical relation [4] and $V_{rev,0}$ (in V) is the reversible voltage at standard pressure condition which is empirically estimated by [5]:

$$V_{rev,0} = 1.5184 - 1.5421 \cdot 10^{-3} T + 9.523 \cdot 10^{-3} T \ln T + 9.48 \cdot 10^{-8} T^2 \quad (S.3)$$

The ohmic overpotential (V_{ohm}), which is caused by the area specific resistance of electrons flowing through electrically conductive components (ASR_{elec} , in $\Omega \cdot \text{cm}^2$) and protons crossing through membrane (ASR_{mem} , in $\Omega \cdot \text{cm}^2$). It is expressed as [6]:

$$V_{ohm} = (ASR_{elec} + ASR_{mem}) \cdot J \quad (S.4)$$

where J (in A/cm²) is the current density. The ASR_{elec} is obtained as one of the fitted parameters in the model calibration. The ASR_{mem} is the major contributor to ohmic resistance and is computed by [7]:

$$ASR_{mem} = \frac{d_{mem}}{\sigma_{mem}} \quad (S.5)$$

where d_{mem} (in cm) is the thickness of the membrane and σ_{mem} (in 1/($\Omega \cdot \text{cm}$)) is the conductivity of membrane, which is modelled by a temperature-dependent Arrhenius expression [1]:

$$\sigma_{\text{mem}} = \sigma_{\text{mem}}^{\text{ref}} \exp \left[\frac{-E_{\text{mem}}^{\text{ohm}} \cdot 10^3}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right] \quad (\text{S.6})$$

where $\sigma_{\text{mem}}^{\text{ref}}$ ($1/(\Omega \cdot \text{cm})$) is the membrane ionic conductivity at the reference temperature T_{ref} (equal to 298.15 K) and $E_{\text{mem}}^{\text{ohm}}$ (in kJ/mol) represents the activation energy for proton transport through membrane.

The concentration overpotential (V_{conc}) is resulted by the reactant depletion and product accumulation in the catalytic sites close to the electrode-electrolyte interface during the water dissociation process. In PEM electrolyzer cell, anodic concentration overpotential dominates over the cathodic one, as large volume of oxygen bubbles produced in anode electrode would block the anodic surface and thus disturb the supply of water to the reaction sites [8]. Moreover, the concentration gradient in the vicinity of the anode caused by slower reaction kinetics of oxygen reduction is another major reason for higher anodic concentration overpotential [9]. Therefore, only the concentration overpotential at the anode is considered:

$$V_{\text{an}}^{\text{conc}} = \frac{R \cdot T}{4 \cdot F} \ln \left(\frac{J_{\text{an}}^{\text{lim}}}{J_{\text{an}}^{\text{lim}} - J} \right) \quad (\text{S.7})$$

where $J_{\text{an}}^{\text{lim}}$ (in A/cm²) is the limiting current density at the anode side.

The activation overpotential (V_{act}) represents the extra voltage required to overcome the activation barrier associated with redox reactions involved in the water electrolysis process. It is calculated based on the Butler-Volmer equation (with $i = \text{an, cat}$) [10]:

$$V_i^{\text{act}} = \frac{R \cdot T}{\alpha_i \cdot F} \operatorname{arcsinh} \left(\frac{J}{2J_i^0} \right) \quad (\text{S.8})$$

where α_i is the charge transfer coefficient which depends on the symmetry of the activation barrier. The exchange current density J_i^0 (in A/cm²) is also modeled through a temperature-dependent Arrhenius equation (with $i = \text{an, cat}$) [11, 12]:

$$J_i^0 = \gamma_i^{\text{R}} \cdot J_i^{0,\text{ref}} \cdot \exp \left[\frac{-E_i^{\text{act}} \cdot 10^3}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right] \quad (\text{S.9})$$

where E_i^{act} (in kJ/mol) is the activation energy required by the electrochemical reaction, $J_i^{0,\text{ref}}$ (in A/cm²) is the exchange current density at reference temperature, and γ_i^{R} is the roughness factor which is calculated based on the catalyst characteristics [13].

Reference

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Table S1 Fixed parameters for 0D electrochemical model of PEM EL cell

Fixed parameters	Symbol	Value
Membrane thickness	t_{mem}/cm	0.0183
Roughness factor at the anode electrode	$\gamma_{\text{an}}^{\text{R}}$	687.82
Roughness factor at the cathode electrode	$\gamma_{\text{cat}}^{\text{R}}$	233.10

Table S2 Fitted parameters for 0D electrochemical model of PEM EL cell

Fitted parameters	Symbol	Value
Activation energy for anode	$E_{\text{an}}^{\text{act}}/(\text{kJ}\cdot\text{mol}^{-1})$	59.95
Activation energy for cathode	$E_{\text{cat}}^{\text{act}}/(\text{kJ}\cdot\text{mol}^{-1})$	8.57
Activation energy for proton transfer	$E_{\text{mem}}^{\text{ohm}}/(\text{kJ}\cdot\text{mol}^{-1})$	10.32
Charge transfer coefficient for anode	α_{an}	0.69
Charge transfer coefficient for cathode	α_{cat}	0.56
Electric ASR	$\text{ASR}_{\text{elec}}/(\Omega\cdot\text{cm}^2)$	7.48×10^{-2}
Reference exchange current density for anode	$J_{\text{an}}^{0,\text{ref}}/(\text{A}\cdot\text{cm}^{-2})$	4.38×10^{-9}
Reference exchange current density for cathode	$J_{\text{cat}}^{0,\text{ref}}/(\text{A}\cdot\text{cm}^{-2})$	4.94×10^{-3}
Reference membrane conductance	$\sigma_{\text{mem}}^{\text{ref}}/(\Omega\cdot\text{cm})^{-1}$	0.106

Table S3 Operating parameters for 0D electrochemical model of PEM EL cell

Operating parameters	Symbol	Value
Current density	$J/(\text{A}\cdot\text{cm}^{-2})$	0–1.8
Limiting current density	$J_{\text{an}}^{\text{lim}}/(\text{A}\cdot\text{cm}^{-2})$	6
Modulation range (% of nominal power of the EL)	-	10%–100%
Operating temperature	$T/^{\circ}\text{C}$	60
Operating pressure	p/bar	30

Table S4 Parameters for power consumption of auxiliaries in the PEM EL system

Parameters	Symbol/Unit	Value
Lower heating value of hydrogen	$\text{LHV}/(\text{kJ}\cdot\text{mol}^{-1})$	240
Motor pump electrical efficiency	η_{wp}	0.75
Power consumption per unit cell area of other auxiliaries (% of nominal power of the EL)	$P_{\text{oa}}(\text{W}\cdot\text{cm}^{-2})$	3.5
Pump total head	$\Delta P_{\text{wp}}/\text{Pa}$	2×10^5
Specific heat capacity of water	$C_p/(\text{J}\cdot\text{g}^{-1}\cdot\text{C}^{-1})$	4.184
Thermoneutral voltage	V_{tn}/V	1.48

Temperature change of the cooling water	$\Delta T/^{\circ}\text{C}$	5
Unit converter from mass to volume	ζ	10^{-6}

Table S5 Parameters for overall problem formulation

Parameters	Symbol	Value
Specific investment cost of the PEM EL	$c_i/(\$/\text{kW})$	1443
Salvage value of the PEM EL (% of Inv. Cost)	-	10%
Daily depreciation cost of the PEM EL	$C_c/\$$	21307
Nominal power of the PEM EL	$P^{e,\text{nom}}/\text{MW}$	60
Lifetime of the PEM EL	Y/year	10
Coal price	$C_{\text{coal}}/(\$\cdot\text{tonne}^{-1})$	103.1
Hydrogen price	$C_{\text{H}_2}/(\$\cdot\text{kg}^{-1})$	4.1
Hydrogen density	$\rho_{\text{H}_2}/(\text{kg}\cdot\text{m}^{-3})$	0.089
Lower heating value of hydrogen	$\text{LHV}_{\text{H}_2}/(\text{MWh}\cdot\text{Nm}^{-3})$	3×10^{-3}
Minimum load factor of the PEM EL	mpl	0.1
Nominal power of the WPP	$P^{\text{w},\text{nom}}/\text{MW}$	150
Characteristic parameters of the wind turbine	m	0.773
	n	8.122