LECTURE 08

Modeling of Electrochemical Processes

Department of Analytical, Colloidal Chemistry and Technology of Rare Elements

Modeling of chemico-technological processes | 6B07102 Chemical Engineering

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Purpose and expected learning outcomes

Purpose: describe whole electrochemical devices (electrolyzers, fuel cells, batteries) with one consistent set of thermodynamic, kinetic and transport equations.

APPLY

Faraday's law to production rates, energy consumption and battery capacity.

CALCULATE

Equilibrium cell voltage from ΔG and the Nernst equation.

CORRECT

Tafel data for uncompensated resistance before extracting kinetic parameters.

DECOMPOSE

A polarization curve into activation, ohmic and mass-transport losses.

SIMULATE

Battery discharge with an equivalent-circuit model and coulomb counting.

VALIDATE

Device models with polarization, HFR, discharge and efficiency data.

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From an electrochemical cell to a device model

01 Define cell

Electrodes, electrolyte, separator, sign convention

02 Thermodynamics

ΔG, E°, Nernst equation

03 Kinetics

Butler–Volmer, Tafel slope, j_0

04 Losses

Ohmic and mass-transport polarization

05 Device model

Electrolyzer, fuel cell, battery

06 Validate

Polarization, discharge, impedance

Industrial relevance: green hydrogen • fuel cells • Li-ion batteries • chlor-alkali • electrowinning

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Faraday's law: from current to product and energy

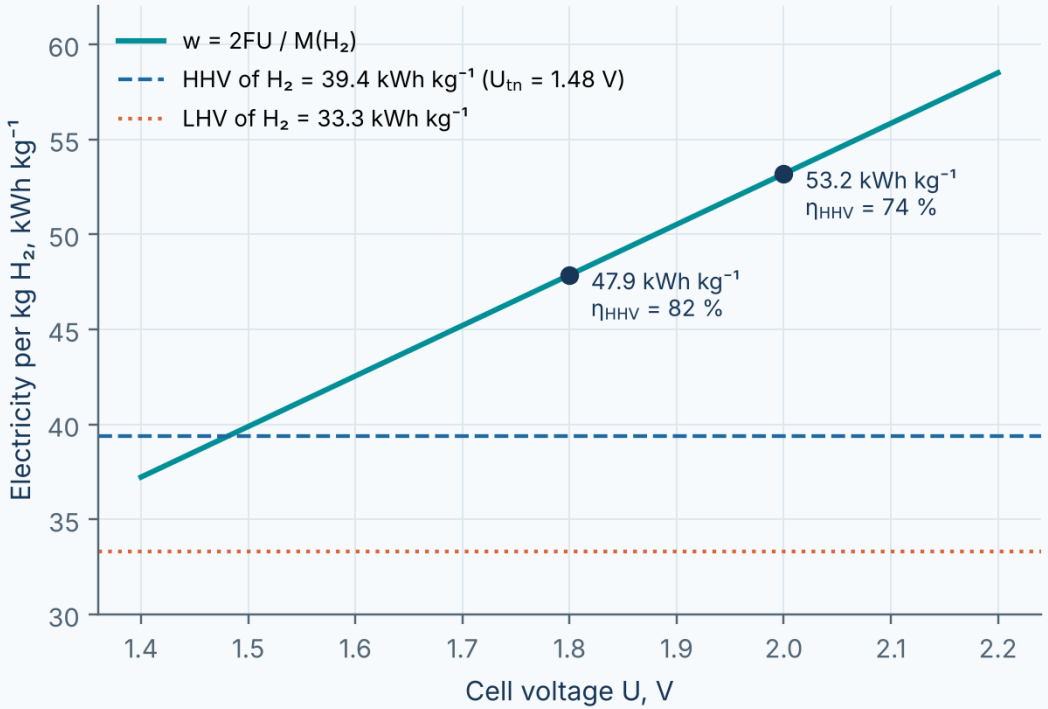
Current fixes the production rate; cell voltage fixes the energy cost.

$$\dot{n} = I / (nF)$$
$$w = nFU / M$$

MODEL CONDITIONS 100 % faradaic efficiency; U is the measured cell voltage, so w already includes every loss.

EXAMPLE Stack of 100 cells at 1000 A produces 3.76 kg H_2 h^{-1}. At 1.8 V the energy cost is 47.9 kWh kg^{-1} (82 % of HHV); at 2.0 V it rises to 53.2 kWh kg^{-1} (74 %).

EXAMPLE · ELECTRICITY PER kg H_2 VS CELL VOLTAGE



ENGINEERING INTERPRETATION Each extra 0.1 V of cell voltage costs 2.66 kWh per kg H_2; voltage losses are operating costs.

Further reading: O'Hayre et al., Fuel Cell Fundamentals, 3rd ed. (2016); Carmo et al., Int. J. Hydrogen Energy 38 (2013) 4901–4934 (PEM water electrolysis).

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Equilibrium cell voltage: the Nernst equation

Thermodynamics sets the voltage at zero current.

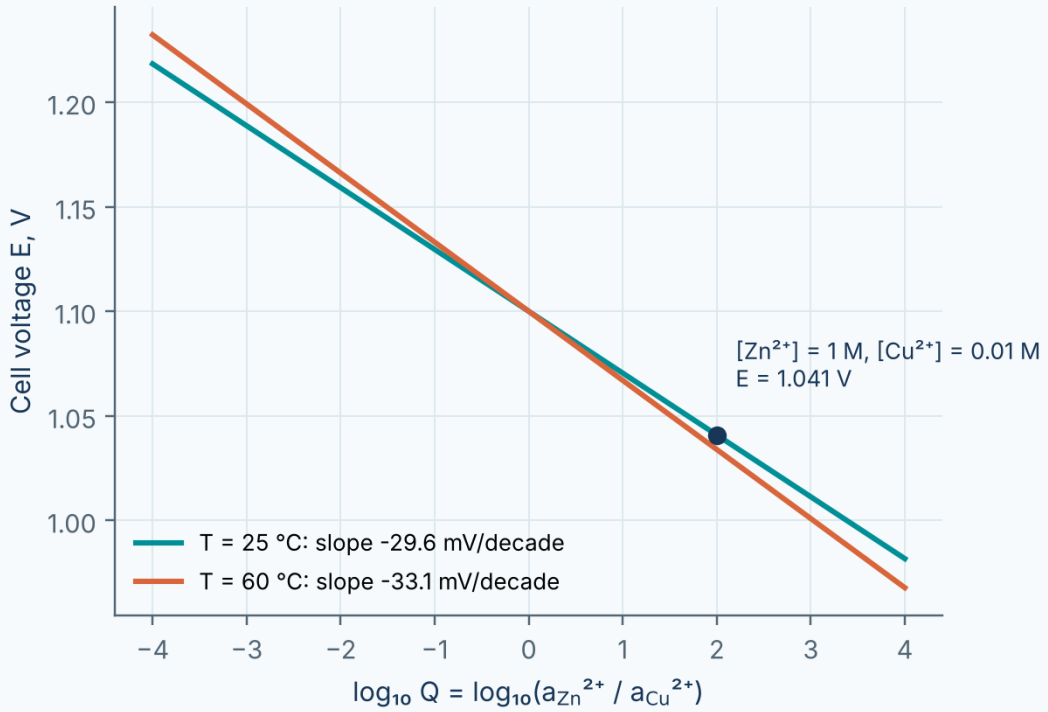
$$\Delta_r G = -nFE$$

$$E = E^\circ - (RT/nF)\ln Q$$

MODEL CONDITIONS Daniell cell Zn | Zn^{2+} || Cu^{2+} | Cu, n = 2, E° = 1.10 V; activities taken as concentrations; E° held constant with T for illustration.

EXAMPLE $[Zn^{2+}]$ = 1 M and $[Cu^{2+}]$ = 0.01 M give E = 1.041 V. The slope is 29.6 mV per decade of Q at 25 °C and 33.1 mV at 60 °C.

EXAMPLE · DANIELL CELL VOLTAGE VS REACTION QUOTIENT



ENGINEERING INTERPRETATION Measured OCV equals E only for a reversible couple after relaxation; junction and mixed potentials shift it.

Further reading: Bard, Faulkner & White, Electrochemical Methods, 3rd ed. (2022), ch. 2–3; Newman & Balsara, Electrochemical Systems, 4th ed. (2021), ch. 1–2, 8.

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Activation and ohmic polarization

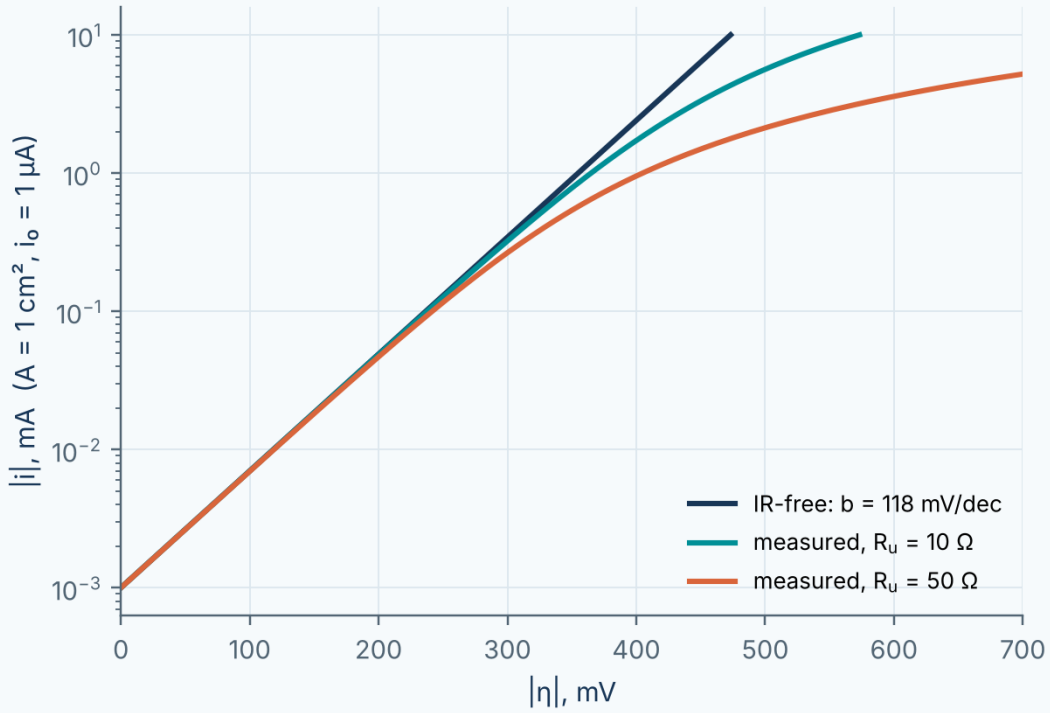
Measured potential contains a kinetic part and a resistive part.

$$\eta = b \log(i/i_0), \quad b = 2.303RT/(\alpha n F)$$
$$E_{meas} = \eta + iR_u$$

MODEL CONDITIONS Cathodic Tafel region, α = 0.5, n = 1, i_0 = 1 µA on 1 cm^2; R_u is the uncompensated solution resistance.

EXAMPLE True slope b = 118 mV/dec. Fitted between 0.1 and 1 mA, R_u = 10 Ω gives an apparent 127 mV/dec and R_u = 50 Ω gives 163 mV/dec.

EXAMPLE · TAFEL PLOT WITH AND WITHOUT IR DROP



ENGINEERING INTERPRETATION Measure R_u (EIS or current interrupt) and correct E before reporting Tafel slopes or α.

Further reading: Bard, Faulkner & White, Electrochemical Methods, 3rd ed. (2022), ch. 2–3; Newman & Balsara, Electrochemical Systems, 4th ed. (2021), ch. 1–2, 8.

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Water electrolyzer: anatomy of the cell voltage

A polarization curve is a sum of separable losses.

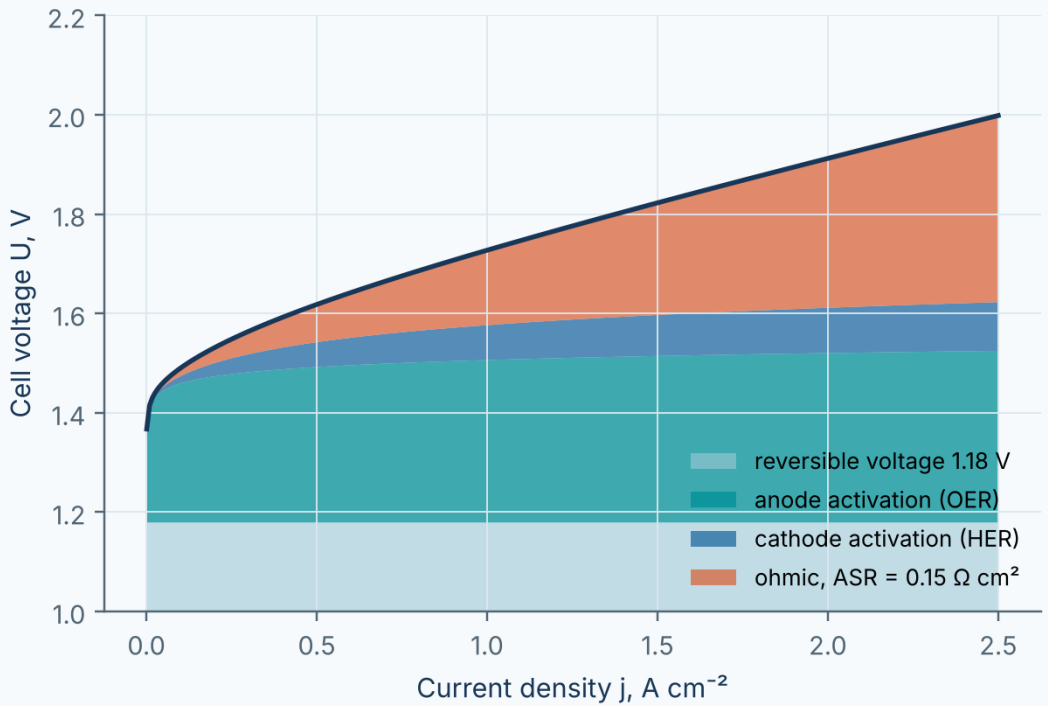
$$U = E_{rev} + \eta_a + \eta_c + j \cdot ASR$$

$$\eta = (RT/\alpha F)\ \mathrm{asinh}(j / 2j_0)$$

MODEL CONDITIONS PEM cell, 80 °C, E_{rev} = 1.18 V. Illustrative: anode $j_0 = 10^{-7}$ A cm^{-2}, α = 1.5; cathode j_0 = 0.1 A cm^{-2}, α = 1; ASR = 0.15 Ω cm^2.

EXAMPLE At 2 A cm^{-2}: U = 1.91 V = 1.18 (reversible) + 0.34 (OER) + 0.09 (HER) + 0.30 V (ohmic).

EXAMPLE · VOLTAGE BREAKDOWN OF A PEM ELECTROLYZER



ENGINEERING INTERPRETATION The OER catalyst and membrane resistance are the two largest levers for lowering U.

Further reading: O'Hayre et al., Fuel Cell Fundamentals, 3rd ed. (2016); Carmo et al., Int. J. Hydrogen Energy 38 (2013) 4901–4934 (PEM water electrolysis).

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Fuel cell: mass-transport limitation and power

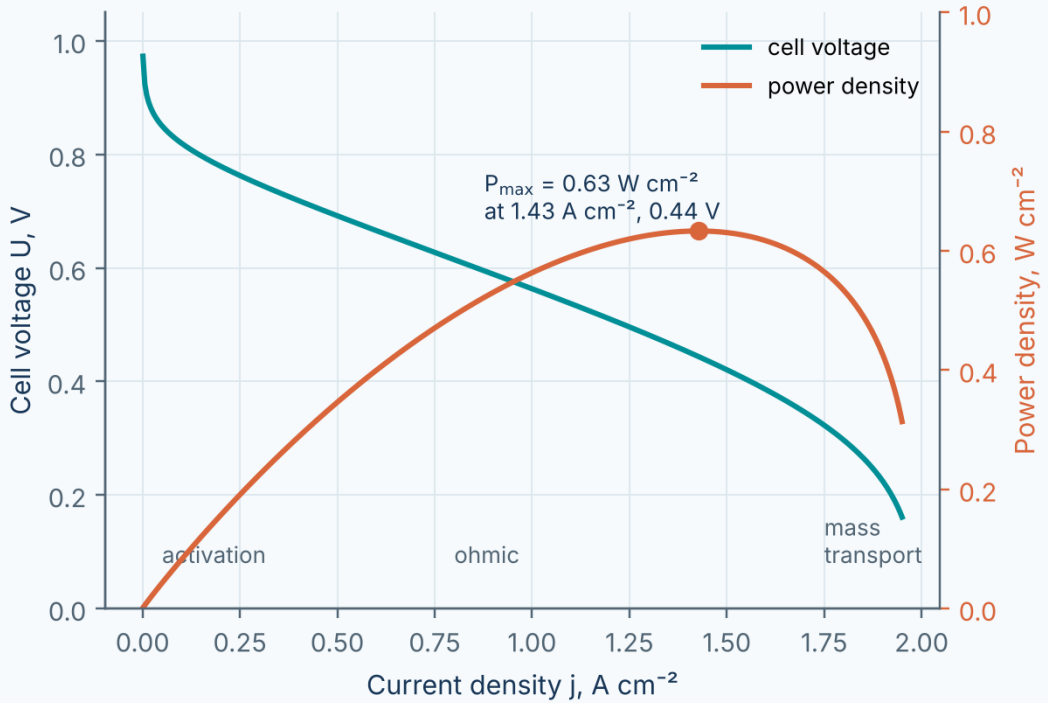
Concentration polarization caps the current a fuel cell can deliver.

$$U = E_{OCV} - \eta_{act} - j \cdot ASR - B \ln[j_L/(j_L - j)]$$
$$P = U \cdot j$$

MODEL CONDITIONS PEM fuel cell, 80 °C, E_{OCV} = 1.0 V, ASR = 0.15 Ω cm^2, limiting current j_L = 2 A cm^{-2}, empirical B = 0.08 V.

EXAMPLE U = 0.56 V at 1 A cm^{-2}. Maximum power 0.63 W cm^{-2} at 1.43 A cm^{-2} and 0.44 V, where efficiency is already low.

EXAMPLE · POLARIZATION AND POWER CURVES



ENGINEERING INTERPRETATION Stacks are usually operated at 0.6–0.7 V, below P_{max}, for efficiency and durability.

Further reading: O'Hayre et al., Fuel Cell Fundamentals, 3rd ed. (2016); Carmo et al., Int. J. Hydrogen Energy 38 (2013) 4901–4934 (PEM water electrolysis).

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Li-ion batteries: capacity from Faraday's law

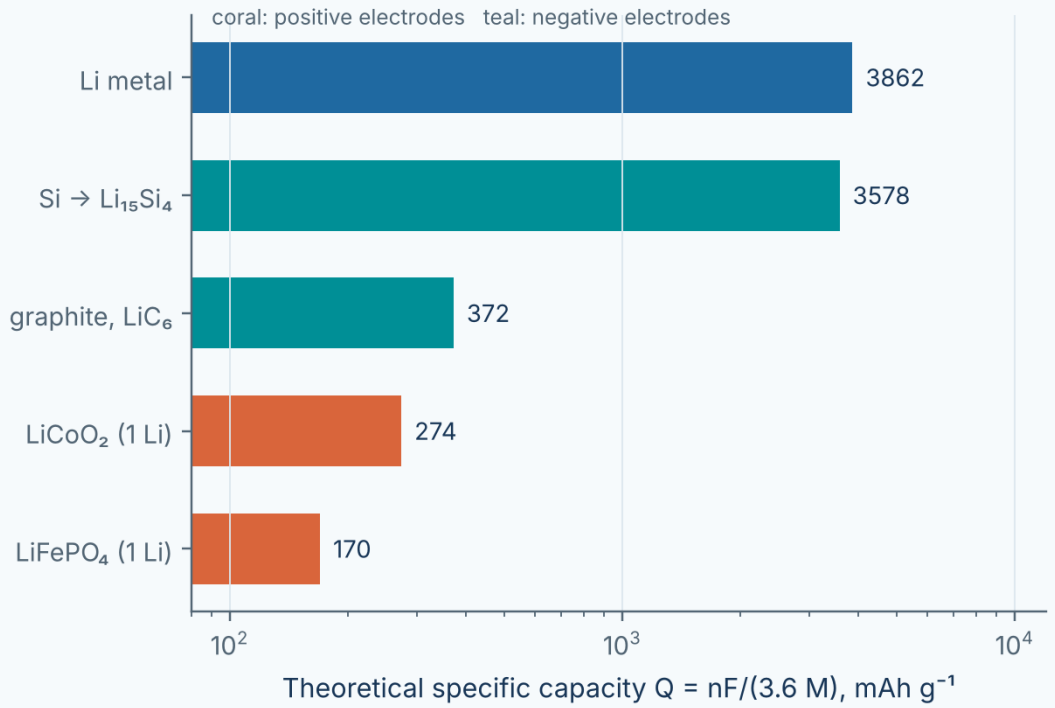
Intercalation hosts store Li^+ and electrons without plating metallic lithium.

$$LiC_6 \rightleftharpoons C_6 + Li^+ + e^-$$
$$Q = nF / (3.6\ M)\ \ [mAh\ g^{-1}]$$

MODEL CONDITIONS Capacity per mass of host material. In practice $LiCoO_2$ cycles only ~0.5 Li, giving ~140 mAh g^{-1}.

EXAMPLE Graphite 372, $LiFePO_4$ 170, $LiCoO_2$ 274 mAh g^{-1}. Silicon ($Li_{15}Si_4$) reaches 3579 mAh g^{-1} but expands by ~300 % in volume.

EXAMPLE · THEORETICAL SPECIFIC CAPACITIES



ENGINEERING INTERPRETATION Cell capacity is set by the limiting electrode and by Li inventory lost to SEI formation.

Further reading: Plett, Battery Management Systems, Vol. 1: Battery Modeling (2015); Doyle, Fuller & Newman, J. Electrochem. Soc. 140 (1993) 1526.

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Battery discharge: equivalent-circuit model

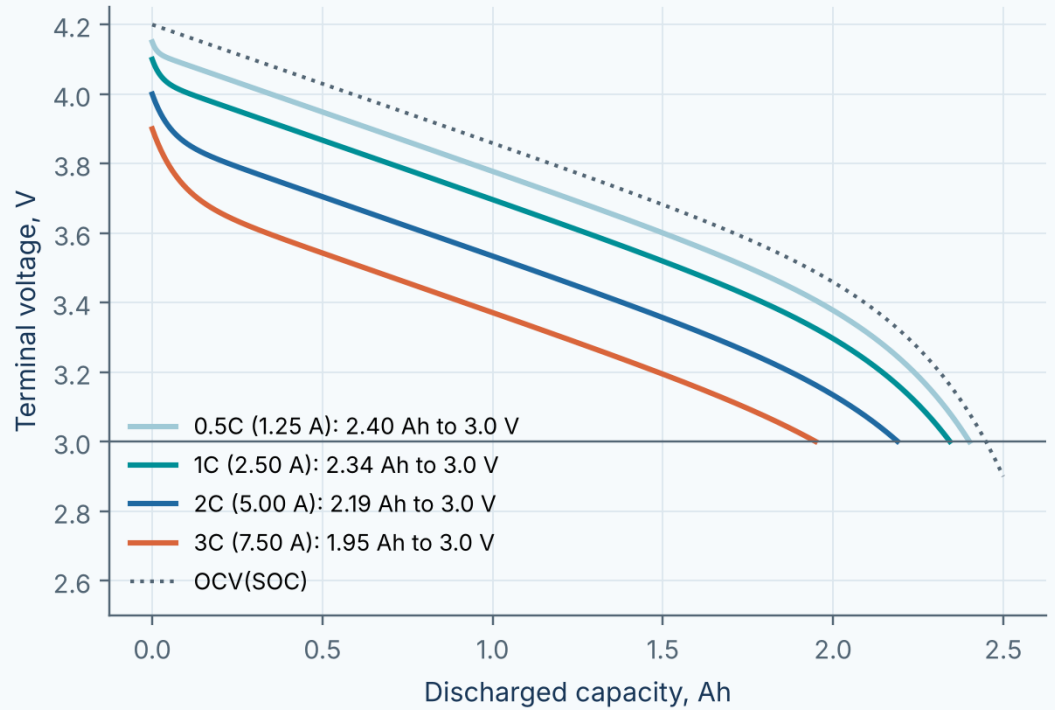
A simple circuit reproduces terminal voltage under load.

$$SOC = SOC_0 - (1/Q_{nom})\int I\,dt$$
$$V = OCV(SOC) - IR_0 - V_1$$

MODEL CONDITIONS 2.5 Ah cell, R_0 = 40 mΩ, R_1 = 25 mΩ, C_1 = 1500 F (τ = 37.5 s), illustrative OCV curve, cut-off 3.0 V, isothermal.

EXAMPLE Delivered capacity: 2.40 Ah at 0.5C, 2.34 Ah at 1C, 2.19 Ah at 2C and 1.95 Ah at 3C (78 %). Higher current reaches the cut-off earlier.

EXAMPLE · DISCHARGE CURVES AT FOUR C-RATES



ENGINEERING INTERPRETATION ECMs run in battery management systems; physics-based (Doyle–Fuller–Newman) models serve cell design.

Further reading: Plett, Battery Management Systems, Vol. 1: Battery Modeling (2015); Doyle, Fuller & Newman, J. Electrochem. Soc. 140 (1993) 1526.

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Validating device models against experiment

Fit parameters on one data set, then predict a different operating condition.

POLARIZATION CURVE

Steady-state points after stabilization; fit j_0, α and ASR on one data set, test on another temperature.

HIGH-FREQUENCY RESISTANCE

EIS or current interrupt gives ASR directly, separating ohmic from kinetic losses.

DISCHARGE AND PULSE TESTS

C-rate series and HPPC pulses give R_0, R_1, C_1; test the model on a drive-cycle profile.

FARADAIC EFFICIENCY

Measure gas volume or GC composition and compare with $I \cdot t/(nF)$.

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Conclusions: a verified model is a useful model

THERMODYNAMICS

ΔG and the Nernst equation give the zero-current voltage only.

KINETICS

Butler–Volmer/Tafel describe activation losses; correct for IR first.

LOSSES

Activation, ohmic and transport losses add up to the measured U.

FARADAY

Current sets production and capacity; voltage sets energy cost.

DEVICE MODELS

Electrolyzer, fuel cell and battery models share the same equations.

APPLICATION

Use models to choose catalysts, membranes and operating points.

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Homework: calculations, interpretation and research

1. THEORY The OCV of a PEM fuel cell is ~1.0 V although E_{rev} = 1.23 V at 25 °C. Give two physical reasons and how each could be included in the model.

2. CALCULATION An electrolyzer of 50 cells × 200 cm^2 runs at 1.5 A cm^{-2} and 1.85 V per cell. Find the H_2 production (kg h^{-1}), the power and the energy per kg H_2.

3. DATA Using slide 6, estimate the apparent Tafel slope for R_u = 25 Ω between 0.1 and 1 mA, then show how IR correction recovers b and i_0.

4. CODE Implement the equivalent-circuit model of slide 10. Find the C-rate at which delivered capacity falls below 80 % and the effect of doubling R_0.

5. RESEARCH Find published polarization curves for PEM electrolyzers with two membrane thicknesses. Estimate ASR from the high-current slope and compare.

Constants: F = 96485 C mol^{-1}; R = 8.314 J mol^{-1} K^{-1}; T = 298.15 K; M(H_2) = 2.016 g mol^{-1}; HHV(H_2) = 39.4 kWh kg^{-1}.

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Recommended Literature

1. Fogler, H. S. *Elements of Chemical Reaction Engineering*. 5th ed., Pearson, 2016.
2. Himmelblau, D. M., Riggs, J. B. *Basic Principles and Calculations in Chemical Engineering*. 8th ed., Pearson, 2012.
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