

BATTERY STORAGE SYSTEMS • 2YBSS

Topic 2

Determination of Open-Circuit Voltage via Thermodynamic Equations

From Gibbs free energy and the Nernst equation to the OCV–SOC relationship

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RECAP & MOTIVATION

From cells to cell voltage

In Topic 1 we saw that a cell stores **electrochemical potential energy** and delivers a voltage set by its chemistry. Now we **quantify that voltage** from thermodynamics.

- ▶ **Open-circuit voltage (OCV)** is the cell's equilibrium voltage with no current flowing.
- ▶ **Thermodynamics** predicts OCV directly from the cell reaction and conditions.
- ▶ **OCV vs. state of charge** is the backbone of battery fuel-gauging (SOC estimation).

ROADMAP OF THIS TOPIC

- 1 Gibbs free energy
- 2 $\Delta G = -nFE$
- 3 Standard potentials E°
- 4 Nernst equation
- 5 Temperature & entropy
- 6 OCV as a function of SOC

TOPIC 2

What you will be able to do

1 Define

State what OCV is and the equilibrium condition behind it.

2 Relate

Link Gibbs free energy to cell voltage via $\Delta G = -nFE$.

3 Compute

Find standard cell voltage E° from half-cell potentials.

4 Apply

Use the Nernst equation for non-standard conditions.

5 Explain

Describe how temperature and entropy affect OCV.

6 Connect

Relate OCV to state of charge for SOC estimation.

DEFINITION

What is open-circuit voltage?

DEFINITION

The **open-circuit voltage (OCV)** is the potential difference across a cell's terminals at **electrochemical equilibrium** — no external current, after the cell has fully rested (relaxed).

It is also called the *electromotive force (EMF)* and represents the maximum voltage the chemistry can deliver.

At rest ($I = 0$)

$$V = OCV$$

Discharging

$$V < OCV$$

Charging

$$V > OCV$$

Current flow adds polarisation (overvoltage); OCV is the reference.

THE KEY RELATIONSHIP

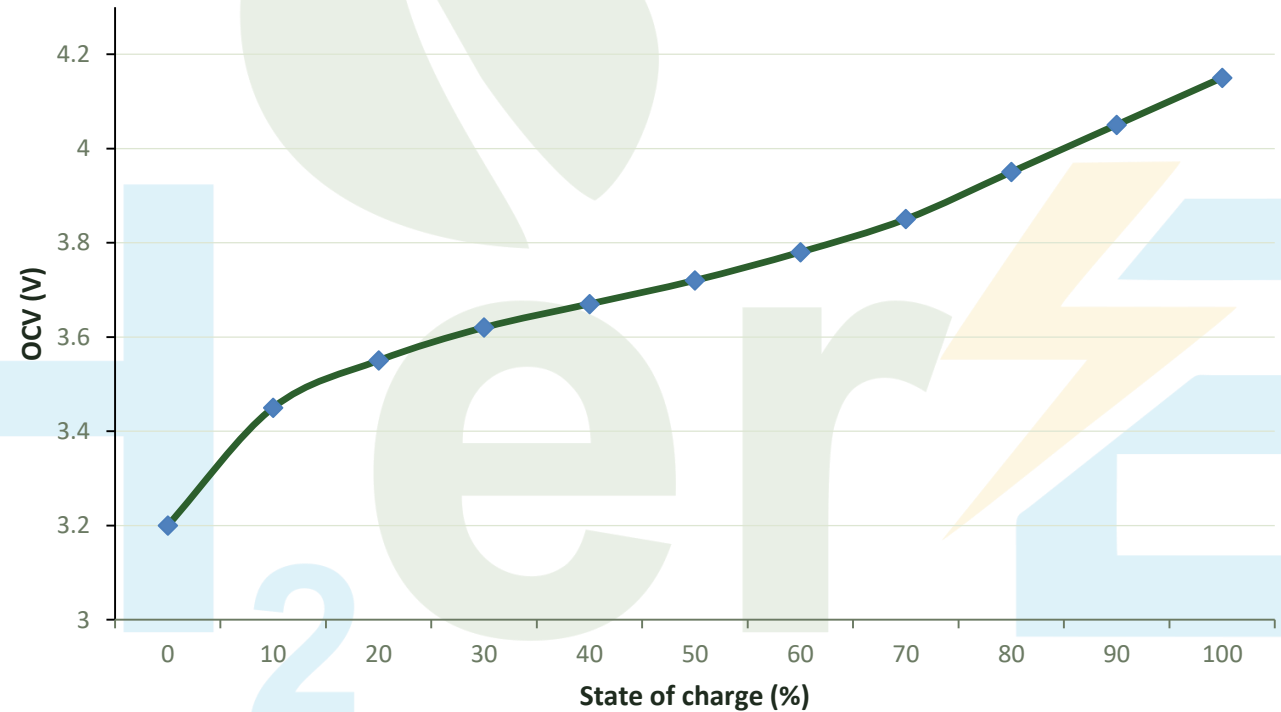
OCV is a function of state of charge

For a cell in equilibrium, OCV is a **static function of state of charge (SOC)**.

A fully charged cell sits at a higher OCV; OCV falls as the cell discharges.

This monotonic curve is what lets us **infer SOC from a rested voltage**.

Example Li-ion OCV vs. SOC



WHAT SETS THE VOLTAGE

Electrode potential

The tendency of a material to **gain or lose electrons** relative to another is its **electrode potential**. The bigger the difference between the two electrodes, the higher the cell voltage.

- ▶ **Negative electrode:** material with low (negative) potential — gives up electrons.
- ▶ **Positive electrode:** material with high (positive) potential — accepts electrons.
- ▶ **Limited by nature:** we can only use elements that exist — strong reducers (left of periodic table) vs. strong oxidisers (right).

STANDARD CELL POTENTIAL

$$E^{\circ}_{\text{cell}} = E^{\circ}_{+} - E^{\circ}_{-}$$

(positive-electrode potential minus negative-electrode potential)

THE DRIVING FORCE

Gibbs free energy

A reaction proceeds spontaneously when its **Gibbs free energy decreases** ($\Delta G < 0$).

ΔG is the **maximum non-expansion (electrical) work** the reaction can deliver — exactly what a battery extracts.

GIBBS FREE ENERGY

$$\Delta G = \Delta H - T\Delta S$$

ΔH

reaction enthalpy (heat content)

T

absolute temperature (K)

ΔS

reaction entropy (disorder)

THE BRIDGE EQUATION

Linking free energy to voltage

All the electrical work comes from the free-energy change, so the equilibrium cell voltage relates directly to ΔG :

FREE ENERGY $\leftrightarrow$ OPEN-CIRCUIT VOLTAGE

$$\Delta G = -n F E_{\text{cell}}$$

n

moles of electrons transferred per reaction

F

Faraday's constant = 96 485 C/mol

E

equilibrium cell voltage (OCV)

Under standard conditions: $\Delta G^\circ = -n F E^\circ$ — a more negative ΔG means a higher cell voltage.

STANDARD POTENTIALS

Building E° from half-cells

Each electrode reaction has a **standard reduction potential** measured against the standard hydrogen electrode (SHE). $E^\circ_{\text{cell}} = E^\circ_+ - E^\circ_-$.

Half-reaction (reduction)	E° vs. SHE
$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$	-3.04 V
$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	-0.76 V
Pb (PbSO_4) negative plate	-0.36 V
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ (SHE)	0.00 V
$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	+0.34 V
PbO_2 (PbSO_4) positive plate	+1.69 V

More negative $\rightarrow$ stronger reducer (anode); more positive $\rightarrow$ stronger oxidiser (cathode).

WORKED EXAMPLE 1

The Daniell cell (Zn–Cu)

Overall: $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$ ($n = 2$ electrons)

1	Negative (anode)	$\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^{-}$	$E^{\circ} = -0.76 \text{ V}$
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2	Positive (cathode)	$\text{Cu}^{2+} + 2\text{e}^{-} \rightarrow \text{Cu}$	$E^{\circ} = +0.34 \text{ V}$
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3	Cell voltage	$E^{\circ} = 0.34 - (-0.76)$	$E^{\circ} = 1.10 \text{ V}$
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4	Free energy	$\Delta G^{\circ} = -nFE^{\circ}$	$\approx -212 \text{ kJ/mol}$
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WORKED EXAMPLE 2

The lead-acid cell



1	Negative plate	$\text{Pb} + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4 + 2\text{e}^-$	$E^\circ = -0.356 \text{ V}$
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2	Positive plate	$\text{PbO}_2 + \dots \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$	$E^\circ = +1.685 \text{ V}$
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3	Cell voltage	$E^\circ = 1.685 - (-0.356)$	$E^\circ = 2.04 \text{ V}$
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A “12 V” car battery = six 2 V lead-acid cells in series. Voltage also varies with acid concentration (SOC) and temperature.

BEYOND STANDARD CONDITIONS

Real cells aren't standard

Standard potentials (E°) assume **specific concentrations (activities) and temperature**. Real OCV drifts from E° as the cell discharges and conditions change — so we need a correction.



Concentration

As reactants are consumed and products build up, the effective driving force changes.



Temperature

Higher T changes the entropy contribution and the equilibrium voltage.



State of charge

Electrode composition shifts with SOC, moving the equilibrium potential.

THE CORRECTION

The Nernst equation

The Nernst equation corrects the standard voltage for actual activities through the **reaction quotient Q**:

NERNST EQUATION

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

R

gas constant 8.314 J/(mol·K)

T

temperature (K)

Q

reaction quotient
(products/reactants)

As products accumulate (Q rises), the $\ln Q$ term grows and the voltage falls.

NERNST — WORKED EXAMPLE

At 25 °C the equation simplifies

AT T = 298 K

$$E = E^{\circ} - (0.0592 / n) \log_{10} Q$$

Because $RT/F \times \ln 10 = 0.0592 \text{ V}$ at 25 °C, each **ten-fold** change in Q shifts the voltage by 0.0592/n volts.

DANIELL CELL EXAMPLE

Given $[\text{Zn}^{2+}] = 0.1 \text{ M}, [\text{Cu}^{2+}] = 1.0 \text{ M}$

Quotient $Q = [\text{Zn}^{2+}]/[\text{Cu}^{2+}] = 0.1$

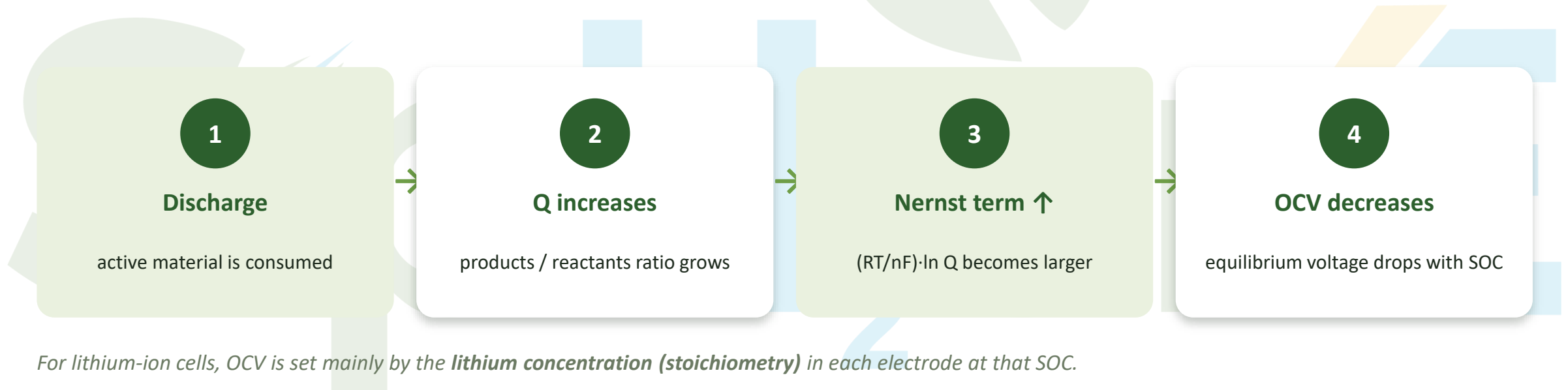
Apply $E = 1.10 - (0.0592/2) \cdot \log(0.1)$

Result $E = 1.10 + 0.030 = 1.13 \text{ V}$

CONNECTING THE DOTS

Why OCV changes with SOC

During discharge, reactant activities **fall** and product activities **rise** — so Q increases and the Nernst term pulls the voltage down. The smooth result is the **OCV–SOC curve**.



TEMPERATURE EFFECTS

OCV and the entropy coefficient

How OCV changes with temperature is set by the **reaction entropy**:

This **entropy coefficient** ($\partial E / \partial T$) is usually small — a few tenths of a mV per °C — but it matters for precise SOC and thermal models.

ENTROPY COEFFICIENT

$$(\partial E / \partial T)_p = \Delta S / (nF)$$

- ▶ Positive $\partial E / \partial T$: OCV rises with temperature
- ▶ Negative $\partial E / \partial T$: OCV falls with temperature
- ▶ Measured by relaxing the cell at several temperatures

ENERGY BALANCE

Where does the heat come from?

Combining the relations gives the full energy picture — useful for **thermal management**:

ENERGY BALANCE

$$\Delta H = \Delta G + T\Delta S$$

REVERSIBLE HEAT

$$q_{\text{rev}} = T\Delta S = nFT(\partial E/\partial T)$$

- ▶ **Useful electrical work** comes from ΔG ($= -nFE$) — the part the battery delivers.
- ▶ **Reversible heat $T\Delta S$** is absorbed or released depending on the sign of the entropy change.
- ▶ **Irreversible heat** (from resistance and kinetics) adds on top — covered in Topic 3.

IN PRACTICE

Measuring OCV

1

Rest & relax

Let the cell sit at zero current until the voltage settles to equilibrium — this can take minutes to hours.

2

Incremental OCV test

Charge/discharge in small steps with long rests, recording the equilibrium voltage at each SOC.

3

Low-current approximation

A very slow (near-C/30) charge/discharge approximates OCV without long waits.

!

Mind hysteresis

Charge-direction OCV differs slightly from discharge-direction OCV — average or model it.

WHY IT MATTERS

OCV is the backbone of SOC estimation

Because OCV maps one-to-one to state of charge, a rested voltage tells the BMS how full the battery is — the foundation of every **voltage-based fuel gauge**.

1

Fuel gauging

Map rested voltage → SOC via the OCV curve.

2

Model anchor

OCV is the reference inside every equivalent-circuit model.

3

Calibration

Rest periods let the BMS re-zero its SOC estimate.

4

Safety limits

Voltage windows are defined relative to OCV.

Dynamic effects under load (resistance, kinetics) are the subject of Topic 3.

CHECK YOURSELF

In-class questions

Q1

A cell reaction transfers $n = 2$ electrons with $E^\circ = 2.0$ V. Compute the standard free-energy change ΔG° .

Q2

Half-cell potentials are $E^\circ_+ = +1.23$ V and $E^\circ_- = -0.83$ V. What is the standard cell voltage?

Q3

At 25 °C a one-electron reaction has $Q = 10$. By how much does the OCV shift from E° ?

Q4

In one sentence, explain why a battery's OCV decreases as it is discharged.

Try Q1 and Q3 with the equations on the board.

WORKED SOLUTIONS

Q1 and Q3 — step by step

Q1 — free energy

Formula $\Delta G^\circ = -nFE^\circ$

Substitute $-(2)(96\,485)(2.0)$

Result $\approx -386 \text{ kJ/mol}$

Negative ΔG° confirms a spontaneous, energy-releasing reaction.

Q3 — Nernst shift

Formula $\Delta E = -(0.0592/n) \cdot \log Q$

Substitute $-(0.0592/1) \cdot \log(10)$

Result $\Delta E = -0.0592 \text{ V}$

OCV is about 59 mV below E° — higher Q lowers the voltage.

(Q2 answer: $E^\circ = 1.23 - (-0.83) = 2.06 \text{ V.}$)

WRAP-UP

Key takeaways

- ▶ OCV is the cell's equilibrium voltage at zero current, after relaxation.
- ▶ Thermodynamics links it to free energy: $\Delta G = -nFE$ ($\Delta G^\circ = -nFE^\circ$).
- ▶ Standard voltage comes from half-cells: $E^\circ_{\text{cell}} = E^\circ(+)-E^\circ(-)$.
- ▶ Worked cells: Daniell ≈ 1.10 V, lead-acid ≈ 2.04 V (both $n = 2$).
- ▶ The Nernst equation corrects for activities: $E = E^\circ - (RT/nF) \ln Q$.
- ▶ Temperature dependence is set by entropy: $(\partial E/\partial T) = \Delta S/(nF)$.
- ▶ OCV maps to state of charge — the foundation of SOC estimation.

Thank you for your attention!

A large, faded version of the SPHERE logo, serving as a background for the slide. It includes the stylized text "SPHERE" with the same green, blue, and yellow color scheme and leaf/lightning bolt motifs.