Thermo-electrochemical generator cells (TEC-G/TREC)

Fundamentals, Heiontec set-up, cycle, energy balances and measurement methods

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Introduction

This script introduces thermo-electrochemical generator cells (TEC-G) and thermally regenerative electrochemical systems (TREC). At its core is the question of how low-temperature heat can be converted into electrical energy in a *physically correct* manner, what limits are imposed by the 2nd law, and how such systems must be measured so that energy balances become reliable.

Didactics. The chapters are structured such that each chapter (a) contains key fundamentals and definitions, (b) provides typical illustrations/sketches, and (c) includes worked examples and derivations. A concrete case study is the Heiontec cell, which we discuss as a TEC-G/TREC system with an Fe/H_2-coupled redox model.

Scientific rigor. Where information is proprietary or not fully specified, we work with clearly marked modeling assumptions and derive only what is thermodynamically mandatory or experimentally verifiable.

Contents

Chapter 1

Motivation and classification of thermo-electrochemical cells

What is this script about?

This script covers **thermo-electrochemical generator cells** (TEC-G) and **thermally regenerative electrochemical systems** (TREC). Both classes exploit the coupling between **heat** and **electrochemical voltage**, to harvest electrical energy from **low-temperature heat** (e. g. waste heat, ambient heat) or, conversely, to provide electrochemical cooling/heating. [1,2]

1.1 Why are TEC-G/TREC cells interesting?

A large fraction of technical energy flows ultimately ends as **heat** at comparatively low temperatures: engines, industrial processes, data centers, power electronics, and building services. Such heat is difficult to utilize because classical heat engines require a large temperature difference to achieve high efficiency.

In this context, TEC-G/TREC cells are interesting because they:

- can operate at **small temperature differences**,
- are, in principle, **scalable** and **flexible in terms of materials**,
- in electrochemical systems, often show **large temperature-dependent potentials**, because these are coupled to **reaction entropies**. [2,3]

One intuitive sentence

In TEC-G/TREC systems, voltage is not only “chemistry”, but also “thermodynamics”: If a redox reaction changes entropy substantially, the cell voltage changes noticeably with the temperature. [1]

1.2 Terms and basic ideas: TEC-G, TREC, thermogalvanic cells

Several closely related terms exist in the literature. In this script we use:

1.2.1 Thermogalvanic cells (thermoelectrochemical cells)

These are cells in which a **temperature difference** ΔT between two electrodes generates a voltage ΔE. An electrochemical **Seebeck coefficient** is often defined as $S_e = \Delta E/\Delta T$. [2,3]

1.2.2 TEC-G (thermo-electrochemical generator)

In this script, the term is used as an **umbrella term** for cells that deliberately use thermal effects for power generation. This can be achieved via:

- a **spatial temperature gradient** (classical thermogalvanic operation) or
- a **temporal temperature fluctuation** (harvesting from temperature cycles)

The latter is also known from intercalation systems. [4]

1.2.3 TREC (thermally regenerative electrochemical cycle/system)

TREC describes a **cycle process**: an electrochemical cell is discharged in one step (power output) and then brought back, via a thermal step (temperature change and thus heat uptake/release), into a state in which it can deliver electrical work again. [1]

Important: “regeneration” is not magic

Regeneration here means:

> The cell returns to an initial composition through a thermally driven step (and, if applicable, internal chemistry/transport processes), so that the discharge process is possible again.

For a cycle to deliver **net work**, the energy balance must be compatible with the 2nd law (see Section 1.4.1). [1, 5]

1.3 Distinction: battery, fuel cell, thermoelectrics, TEC-G/TREC

Many misunderstandings arise because, in practice, TEC-G/TREC cells are measured “like a battery” (voltage, current, power), yet from a physics perspective they must partly be classified differently.

1.3.1 Comparison table (qualitative)

Table 1.1 provides a qualitative comparison of the fundamental differences between these energy converters.

Technology	Primary energy source	Typical driving force	Characteristic
Battery	chemical potential difference (internal)	ΔG of the reaction	discharges until chemical equilibrium
Fuel cell	chemical fuel (supplied externally)	ΔG from continuous feed	steady-state operation possible
Thermoelectrics	heat flow between T_{hot} and T_{cold}	Seebeck effect in a solid	no reaction chemistry, often small S
TEC-G/TREC	heat + electrochemical entropy/composition	$\partial E/\partial T$, transport/regeneration	leverages large reaction entropies; cyclic or gradient-driven

Table 1.1: Rough distinction: battery vs. fuel cell vs. thermoelectrics vs. TEC-G/TREC (qualitative).

1.3.2 Concept map

The conceptual connections between energy source and converter type are summarized in Figure 1.1.

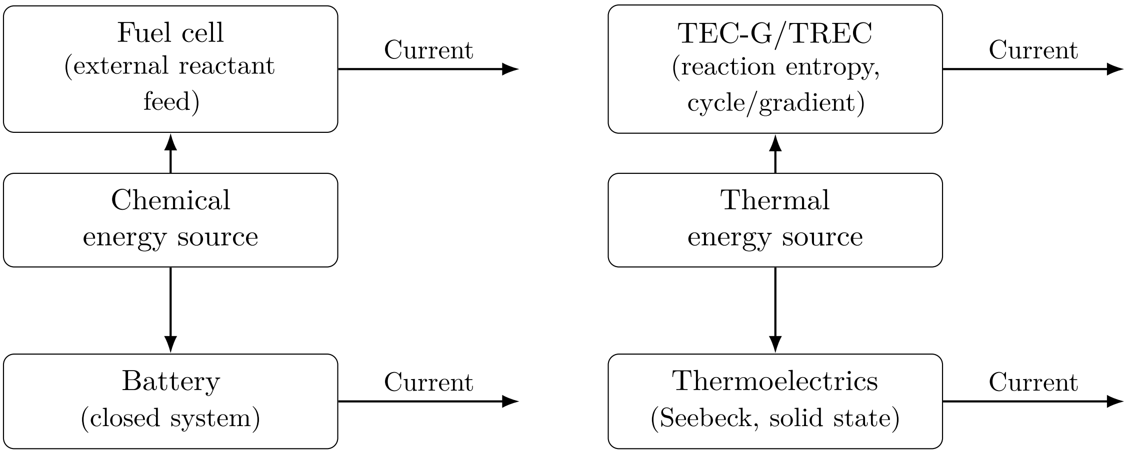

Figure 1.1: Concept map: Which energy source primarily drives which technology? (qualitative)

1.4 Common questions and misconceptions

1.4.1 Is this a "perpetual motion machine"?

In short: **no** — at least not if the physics is accounted for correctly. A system that operates cyclically (i.e., ends up in the initial state again) and still delivers **net work** to the outside must exploit an **external driving force**:

- either an effective temperature difference (spatial or temporal),
- or a mass/chemistry flux (e. g. gas uptake, corrosion, side reactions),
- or another non-equilibrium source (radiation, humidity gradients, etc.).

The 2nd law sets limits: from heat at *nearly the same temperature* one can only obtain work with a very low maximum efficiency. [5]

Remember: small $\Delta T \Rightarrow$ low efficiency

If the temperature difference is small, the maximum (Carnot) efficiency is small. Thus, for a given electrical power, a **comparatively large heat flow** is required. This is not a weakness of a particular material, but a consequence of thermodynamics.

1.4.2 Where does the energy come from if the cell is "just sitting there"?

Two typical possibilities (and both should be checked experimentally):

1. **Ambient heat** is converted into electrical energy by the cell internally creating/using a temperature difference (TREC/fluctuation harvesting). [1,4]
2. **Chemical energy** is (unnoticed) consumed, e. g. through side reactions, gas uptake/release, electrode corrosion, or irreversible conversion of organic additives. Then the system would be closer to a (not fully recognized) battery/fuel cell.

1.5 Orders of magnitude: why ΔT matters so much

This section provides two quick back-of-the-envelope calculations to build intuition for the orders of magnitude. The calculations are intentionally simple; energy balances will be formalized in later chapters.

1.5.1 Example calculation 1.1: Carnot limit for a small temperature difference

Example 1.1 (Carnot): $\Delta T = 5\,\mathrm{K}$ at room temperature

Assume a cell effectively operates between

$$T_{\mathrm{amb}} = 300\,\mathrm{K}, \qquad T_{\mathrm{cold}} = 295\,\mathrm{K}.$$

The maximum possible heat-engine efficiency is

$$\eta_{\mathrm{Carnot}} = 1 - \frac{T_{\mathrm{cold}}}{T_{\mathrm{amb}}} = 1 - \frac{295}{300} \approx 0.0167 \approx 1{,}7\,\%.$$

Interpretation: Even a perfect system could, for this temperature lift, convert at most about 1,7 % of the absorbed heat into work.

1.5.2 Example calculation 1.2: heat flow corresponding to an electrical power

Example 1.2: 10 mW electrical power at 1 % efficiency

Let us optimistically assume a TEC-G/TREC system reaches $\eta = 1\,\%$. For an electrical power of

$$P_{\mathrm{el}} = 10\,\mathrm{mW}$$

at least a heat flow of

$$\dot{Q}_{\mathrm{in}} \approx \frac{P_{\mathrm{el}}}{\eta} = \frac{0.010}{0.01} = 1\,\mathrm{W}$$

must enter the system.

Interpretation: Low efficiency is not automatically "bad": If waste heat is available anyway and the application only needs small powers, this can still make sense. At the same time, the calculation shows why good heat transfer and measurement methods are so crucial.

1.6 Placing the Heiontec cell within the scope of this script

In the following chapters we use a concrete TEC-G cell (Heiontec) as a **case study**, in order to

- discuss its design and selective electrode reactions,
- formulate a mechanistic cycle,
- check energy balances against the 2nd law,
- and describe measurement methods so that results can be interpreted reproducibly.

Important: this script is **not a product brochure**. The goal is a **physically consistent** and **experimentally testable** presentation.

1.7 Brief conclusion

Take-aways

1. TEC-G/TREC systems couple heat and electrochemical voltage via **reaction entropies**.
2. Cyclic net energy output is only possible if an **external driving force** (typically heat flow/temperature swing) is exploited.
3. For small temperature differences, the **theoretical efficiency limits are small**: correspondingly, electrical power requires heat flow.
4. Consequently, **energy balances and clean measurement methods** are essential.

Chapter 2

Thermodynamic and electrochemical fundamentals

Learning objectives of this chapter

This chapter provides the **physical foundation** for TEC-G/TREC cells:

- why the **cell voltage** is directly linked to **Gibbs free energy**,
- how the **Nernst equation** follows from chemical potentials,
- why the **temperature coefficient** $\partial E/\partial T$ is an **entropy signature**,
- and which **heat effects** occur during discharge/regeneration (reversible vs. irreversible).

This later enables us to derive **mechanistic cycles** and **energy balances** for specific TEC-G/TREC cells (e. g. Heiontec) in a rigorous way.

2.1 State variables, laws of thermodynamics, and chemical potential

We consider an electrochemical cell as a **thermodynamic system** with the state variables temperature T, pressure p, amounts of substance n_i, and, if applicable, electric charge. The first two laws in a form useful to us are:

$$\text{First law:} \quad dU = \delta Q + \delta W \tag{2.1}$$

$$\text{Second law (reversible):} \quad \delta Q_{\text{rev}} = T\,dS \tag{2.2}$$

Here, U is the internal energy and S is the entropy. In chemistry it is often more practical to work with the potentials **enthalpy** H and **Gibbs free energy** G:

$$H = U + pV \tag{2.3}$$

$$G = H - TS = U + pV - TS \tag{2.4}$$

2.1.1 The chemical potential

The **chemical potential** μ_i describes how G changes with the amount of substance:

$$\mu_i \equiv \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j\neq i}}. \tag{2.5}$$

For ideal solutions, or as a starting point, we have:

$$\mu_i = \mu_i^\circ + RT \ln a_i, \tag{2.6}$$

where a_i is the **activity** (not necessarily equal to the concentration!).

Remember: activities rather than concentrations

As soon as strong ion–ion interactions, high ionic strengths, or **complex formation** occur, the *activity* a_i governs the thermodynamics. In TEC-G/TREC systems this is particularly important because solvation and complexation can strongly influence ΔS (and thus $\partial E/\partial T$). [2,3]

2.2 Why does $E = -\Delta G/(nF)$ hold?

The central bridge between thermodynamics and electrochemistry is:

$$E_{\mathrm{rev}} = -\frac{\Delta G}{nF}. \tag{2.7}$$

2.2.1 Derivation via maximum non-pV work

At constant T and p, the maximum obtainable **non-expansion work** $W_{\mathrm{nonPV,max}}$ (i.e., everything except $p\,dV$ work) equals the negative change in Gibbs free energy:

$$W_{\mathrm{nonPV,max}} = -\Delta G. \tag{2.8}$$

In a galvanic cell, the relevant non-pV work is the **electrical work** in the external circuit. Per mole of reaction, n electrons are transferred, so the charge is

$$Q = nF \tag{2.9}$$

($F \approx 96\,485\,\mathrm{C/mol}$). The reversible electrical work is

$$W_{\mathrm{el,rev}} = Q\,E_{\mathrm{rev}} = nFE_{\mathrm{rev}}. \tag{2.10}$$

Equating the two directly yields (2.7). [5,6]

Interpretation

EMF/open-circuit voltage is not "mystical battery content", but a measure of how strongly a defined cell reaction at a given T and composition *could* convert Gibbs free energy into electrical work (reversibly, without losses).

2.3 Nernst equation: composition → voltage

2.3.1 Half-cell potential from chemical potentials

Consider a general redox half-reaction

$$\mathrm{Ox} + n\,\mathrm{e}^- \rightleftharpoons \mathrm{Red}. \tag{2.11}$$

At equilibrium, the electrochemical potentials are balanced. For the resulting electrode-potential equation one obtains

$$E = E^\circ + \frac{RT}{nF} \ln\left(\frac{a_{\mathrm{Ox}}}{a_{\mathrm{Red}}}\right). \tag{2.12}$$

[6,7]

2.3.2 Cell voltage

For an overall cell reaction with reaction quotient Q we obtain

$$E = E^{\circ} - \frac{RT}{nF} \ln Q. \tag{2.13}$$

Remember: 59 mV per decade at 25 °C

For $T = 298{,}15\,\mathrm{K}$ we have

$$\frac{RT}{F} \ln 10 \approx 59{,}16\,\mathrm{mV}.$$

For a 1-electron reaction ($n = 1$), a factor of 10 in the activity ratio shifts the potential by $\approx 59\,\mathrm{mV}$.

2.3.3 Example calculation 2.1: concentration/activity change

Example 2.1 (Nernst): potential shift due to activity ratio

Consider a 1-electron half-reaction ($n = 1$) at 25 °C. How much does E change if $\frac{a_{\mathrm{Ox}}}{a_{\mathrm{Red}}}$ increases from 1 to 10?

From (2.12) it follows

$$\Delta E = \frac{RT}{F} \ln(10) \approx 59{,}16\,\mathrm{mV}.$$

Result: The potential increases by about 59 mV.

2.4 Temperature coefficient and reaction entropy

TEC-G/TREC cells rely on the fact that E changes with T. The starting point is again (2.7) and the thermodynamic identity

$$\left(\frac{\partial G}{\partial T}\right)_{p,\{a_i\}} = -S. \tag{2.14}$$

For a cell reaction it follows (for constant activities):

$$\left(\frac{\partial \Delta G}{\partial T}\right)_{p,\{a_i\}} = -\Delta S. \tag{2.15}$$

Differentiating $E = -\Delta G/(nF)$ yields:

$$\left(\frac{\partial E}{\partial T}\right)_{p,\{a_i\}} = \frac{\Delta S}{nF}. \tag{2.16}$$

[1, 2]

2.4.1 Physical meaning

- $\Delta S > 0 \Rightarrow \partial E/\partial T > 0$: higher temperature increases the EMF.
- $\Delta S < 0 \Rightarrow \partial E/\partial T < 0$: higher temperature decreases the EMF.

In thermogalvanic cells, the **Seebeck coefficient** S_e is often defined as

$$S_e = \frac{\Delta E}{\Delta T} \approx \frac{\Delta S}{nF}. \tag{2.17}$$

[3]

2.4.2 Example calculation 2.2: ΔS from dE/dT

Example 2.2 (entropy from temperature coefficient)

Assume a redox couple exhibits a linear temperature coefficient in a relevant range, $\frac{dE}{dT} = 1{,}5\,\mathrm{mV/K}$ for $n = 1$.
Then

$$\Delta S = nF\frac{dE}{dT} = 1 \cdot 96\,485\,\mathrm{C/mol} \cdot 1{,}5 \cdot 10^{-3}\,\mathrm{V/K} \approx 145\,\mathrm{J/(mol\,K)}.$$

At $T = 298\,\mathrm{K}$ this corresponds to a reversible amount of heat

$$Q_{\mathrm{rev}} = T\Delta S \approx 298\,\mathrm{K} \cdot 145\,\mathrm{J/(mol\,K)} \approx 43\,\mathrm{kJ/mol}.$$

Interpretation: If the cell operates under load faster than heat can flow in, a noticeable “self-cooling” can occur.

2.5 Heat effects in electrochemical cells

When a current flows, a cell can become **cold** or **warm**—depending on the sign and magnitude of the reversible and irreversible contributions.

2.5.1 Reversible: entropic (Peltier-like) electrode heat

In the reversible limit, the heat absorbed/released per unit time is directly linked to $\partial E/\partial T$:

$$\dot{Q}_{\mathrm{rev}} = I\,T\left(\frac{\partial E_{\mathrm{rev}}}{\partial T}\right). \tag{2.18}$$

[6]

Important: $\dot{Q}_{\mathrm{rev}}$ can be positive or negative.

- $\dot{Q}_{\mathrm{rev}} > 0$: The cell **absorbs heat** (cools).
- $\dot{Q}_{\mathrm{rev}} < 0$: The cell **releases heat** (heats up).

2.5.2 Irreversible: overpotentials and ohmic losses

Real cells operate at a terminal voltage V that during discharge typically lies below the reversible EMF: $V < E_{\mathrm{rev}}$. The difference represents losses (activation, concentration, ohmic) and is converted to heat:

$$\dot{Q}_{\mathrm{irr}} = I\,(E_{\mathrm{rev}} - V) \quad \geq 0. \tag{2.19}$$

2.5.3 Net: when does a cell cool?

We define the *net* heat absorbed into the cell as

$$\dot{Q}_{\mathrm{cell}} = \dot{Q}_{\mathrm{rev}} - \dot{Q}_{\mathrm{irr}}. \tag{2.20}$$

Then:

- $\dot{Q}_{\mathrm{cell}} > 0$: net heat uptake $\Rightarrow$ **cooling**,
- $\dot{Q}_{\mathrm{cell}} < 0$: net heat release $\Rightarrow$ **heating**.

Example 2.3 (heat balance during operation)

Assume $I = 0{,}10\,\mathrm{A}$, $T = 298\,\mathrm{K}$, and $\frac{\partial E}{\partial T} = 1{,}0\,\mathrm{mV/K}$. Then

$$\dot{Q}_{\mathrm{rev}} = IT\frac{\partial E}{\partial T} = 0.10 \cdot 298 \cdot 0.001 \approx 0{,}0298\,\mathrm{W}.$$

If the cell loses $E_{\mathrm{rev}} - V = 0{,}20\,\mathrm{V}$ under load, then

$$\dot{Q}_{\mathrm{irr}} = I(E_{\mathrm{rev}} - V) = 0.10 \cdot 0.20 = 0{,}020\,\mathrm{W}.$$

Thus

$$\dot{Q}_{\mathrm{cell}} \approx 9{,}8\,\mathrm{mW} > 0 \Rightarrow \text{Cell cools.}$$

2.5.4 Context: Seebeck, Peltier and Thomson

- **Seebeck effect** (): a temperature difference generates a voltage in solid-state thermoelectrics.

- **Peltier effect** (): a current across a junction can absorb/release heat. In electrochemical cells, the reversible electrode heat (2.18) is the most important analog concept.

- **Thomson effect** (): current in a conductor *with a temperature gradient* generates/absorbs reversible heat along the conductor. For electrochemical self-cooling it is usually *not* the primary mechanism (reaction entropy + losses dominate).

2.6 Mini guide: which measurement yields which parameter?

Measured quantity	Directly yields	Typical pitfalls
Open-circuit voltage $E_{\mathrm{OC}}(T)$	$\partial E/\partial T \Rightarrow \Delta S$ via (2.16)	true isothermality, drift, reference electrodes, changes in activity
I–V curve / load step	R_{int}, overpotentials, maximum power	polarization, mass transport, pseudocapacitance
Temperature profile $T(t)$ under load	indications of $\dot{Q}_{\mathrm{cell}}$ (2.20)	heat transfer dominates, sensor offset/lag
Calorimetry / heat flow	energy balance Q vs. $\int VI\,dt$	calibration, heat losses, boundary conditions

Table 2.1: Measured quantities and their physical meaning (in preparation for Chapters 5/6).

2.7 Quick recap

Take-aways

1. **Voltage is free energy:** $E = -\Delta G/(nF)$ (reversible).
2. **Composition matters through activities:** Nernst (2.13).
3. **Temperature coefficient is entropy:** $\partial E/\partial T = \Delta S/(nF)$.
4. **Cooling/heating is accounted for by balances:** $\dot{Q}_{\mathrm{cell}} = \dot{Q}_{\mathrm{rev}} - \dot{Q}_{\mathrm{irr}}$.
5. These relationships are the basis for **TEC-G/TREC cycles**, energy balances, and measurement methods.

Chapter 3

Structure and chemistry of the Heiontec cell

Learning objective of this chapter

We describe the Heiontec cell as a **concrete example** of a TEC-G/TREC cell:

- which **components** (electrodes, electrolyte, housing) are publicly described,
- which **redox system** (Fe^{3+}/Fe^{2+} and H_2/H^+) is assumed,
- how **ion selectivity** and **blocking** enforce a defined cell reaction,
- and how **stoichiometric** relationships (charge ↔ amount of substance converted) can be derived from this.

The focus is on a **scientifically verifiable** description. Where details are proprietary, we state this explicitly.

3.1 Sources and model limitations

The structure described below and the chemical functional assignment are based on:

- the publicly available **explanatory model** "HFe01ST TEC-G" from HEIONTEC/HEIONIT [8],
- the public technology/overview page of HEIONTEC [9],
- as well as general literature on iron electrolytes, H_2 side reactions, and "rebalancing" in iron flow batteries [10, 11].

Transparency note

Some terms in the Heiontec model (e. g. "modified polyols", "set to reducing") are **not fully specified**. For this script, we therefore treat these components as **functional building blocks** (complexation, redox buffer, proton/H_2 storage) and derive only what necessarily follows from thermodynamics and the published stoichiometry.

3.2 Schematic cell design

The explanatory model describes a cell with two electrodes that dip into a **liquid electrolyte** in a **sealed vessel** [8]:

- a **carbon-based electrode** (C electrode),
- an **iron-based electrode** (Fe electrode, “passivated”),
- electrolyte with Fe^{2+}, Fe^{3+}, H^+, H_2 and “modified polyols”. [8]

3.2.1 Sketch: components and current flow

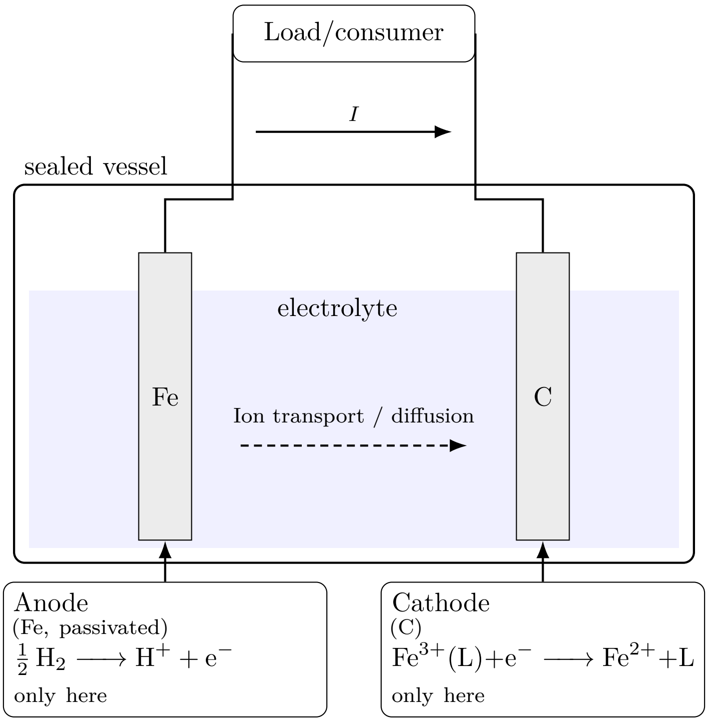

Figure 3.1: Schematic structure of the Heiontec cell according to the published explanatory model: two electrodes in a sealed vessel, liquid electrolyte, external circuit through a load. The electrolyte contains $Fe^{2+}, Fe^{3+}, H^+, H_2$ as well as polyols/complexes. Selectivity (“only here”) is a key design principle. [8]

3.3 Electrolyte: Fe^{2+}/Fe^{3+}, H_2/H^+ and modified polyols

The published model explicitly names the components contained in the electrolyte [8]:

1. **Fe^{2+} ions** and **Fe^{3+} ions** as a redox couple,
2. **H^+** and **H_2** as a second redox couple,
3. **modified polyols** (set to reducing), which
    - complex Fe^{3+} and
    - can take up and release H^+/H_2.

3.3.1 Why is this chemically plausible?

Two aspects are well known in aqueous iron electrolytes:

- Fe^{3+} is prone to hydrolysis and precipitation in many pH ranges (e. g. $Fe(OH)_3$); therefore ligands/complexes and pH management play a major role. [11]

- At negative potentials, hydrogen evolution (HER) is often a competing side reaction; in iron flow systems, “rebalancing” or recombination of H_2 with Fe^{3+} is therefore actively investigated. [10, 11]

3.4 Ion selectivity and blocking of the overall reaction

The explanatory model describes an **ion-selective** design [8]:

- **Fe^{3+} complexes** can react **only at the C electrode**.
- **H_2/H^+** can react **only at the surface of the passivated Fe electrode**.

3.4.1 What does “passivated” mean in the model context?

In the present model, the Fe electrode is not primarily “iron as reactant”, but acts as a **reaction-selective site** for the H_2/H^+ half-reaction. A passivation layer can (qualitatively) fulfill three tasks:

1. suppression of direct Fe corrosion/Fe dissolution,
2. prevention of direct, uncontrolled contact between Fe^{3+} complexes and the metallic surface (self-discharge),
3. provision of a defined interface for H_2 oxidation/proton formation.

Why is selectivity so important?

Without selectivity, the (thermodynamically possible) redox reaction $Fe^{3+} + \frac{1}{2} H_2 \longrightarrow Fe^{2+} + H^+$ could proceed *directly* in the electrolyte or on arbitrary surfaces. Then there would be chemistry, but no controlled electron flow through the external circuit. The central idea is therefore: **force** the electrons through the load. [8]

3.5 Formal redox system and cell reaction

3.5.1 Overall reaction (as given in the model)

The explanatory model names, as the “blocked cell reaction”, a “rebalancing” reaction known from iron flow batteries [8]:

$$Fe^{3+} + \frac{1}{2} H_2 \longrightarrow Fe^{2+} + H^+. \tag{3.1}$$

In the flow-battery literature, recombination of hydrogen with Fe^{3+} is likewise discussed as capacity/SoC restoration. [10]

3.5.2 Half-reactions and electron balance

A consistent split (in acidic medium) is:

At the Fe electrode (in the discharge step: oxidation of hydrogen)

$$\frac{1}{2} H_2 \longrightarrow H^+ + e^-. \tag{3.2}$$

At the C electrode (reduction of Fe^{3+} to Fe^{2+})

$$\mathrm{Fe}^{3+} + \mathrm{e}^- \longrightarrow \mathrm{Fe}^{2+}. \tag{3.3}$$

Adding (3.2) and (3.3) directly yields (3.1). Thus, the number of electrons per overall reaction is $n = 1$. (See Chapter 2.)

3.5.3 Complexed species: symbolic notation

The model explicitly speaks of Fe^{3+} **complexes** and an "opening" of these complexes with an increase in entropy [8]. Without knowing the ligand structure, we write formally:

$$\mathrm{Fe}^{3+}(\mathrm{L}) + \mathrm{e}^- \longrightarrow \mathrm{Fe}^{2+} + \mathrm{L}, \tag{3.4}$$

where L denotes the ligand/polyol component.

Bridge to Chapter 2: entropy as a signature

If, during the reduction of $Fe^{3+}(L)$, ligands are released and the number of microscopic states in the electrolyte increases, a positive contribution to ΔS is plausible. Via $\partial E/\partial T = \Delta S/(nF)$ (Chapter 2) this results in **thermally** relevant cell behavior.

3.6 Stoichiometry: charge ↔ amount of substance converted

From $n = 1$ it follows immediately (Faraday):

$$n_{\mathrm{Fe}^{3+}} = \frac{Q}{F}, \qquad n_{\mathrm{Fe}^{2+}} = \frac{Q}{F}, \qquad n_{\mathrm{H}^+} = \frac{Q}{F}, \qquad n_{\mathrm{H}_2} = \frac{Q}{2F}. \tag{3.5}$$

3.6.1 Example calculation 3.1: material conversion for a discharge

Example 3.1: 10 mA for 10 min

A cell delivers $I = 10\,\mathrm{mA}$ for $t = 10\,\mathrm{min}$. Then the delivered charge is

$$Q = It = 0.010 \cdot (600) = 6\,\mathrm{C}.$$

Thus:

$$n_{\mathrm{Fe}^{3+}} = \frac{6}{96485} \approx 6{,}2 \cdot 10^{-5}\,\mathrm{mol}, \qquad n_{\mathrm{H}_2} = \frac{6}{2 \cdot 96485} \approx 3{,}1 \cdot 10^{-5}\,\mathrm{mol}.$$

As a gas volume (rough orientation, ideal-gas assumption at 25 °C, 1 bar):

$$V_{\mathrm{H}_2} \approx nRT/p \approx 3.1 \times 10^{-5} \cdot \frac{8.314 \cdot 298}{10^5} \approx 0{,}77\,\mathrm{mL}.$$

Interpretation: Even at small currents, measurable conversions can occur (Fe^{3+}/Fe^{2+}, pH shift, H_2 inventory).

3.6.2 Example calculation 3.2: pH change as a plausibility check

Example 3.2: pH shift without buffer (order of magnitude only)

Assume the electrolyte volume is $V = 10\,\mathrm{mL}$ and the cell delivers $Q = 6\,\mathrm{C}$ as in Example 3.1. Then the produced amount of H^+ is

$$\Delta n_{\mathrm{H}^+} = \frac{Q}{F} \approx 6{,}2 \cdot 10^{-5}\,\mathrm{mol}.$$

Without buffer/complex binding, this yields a concentration change

$$\Delta c_{\mathrm{H}^+} = \frac{\Delta n}{V} \approx \frac{6.2 \times 10^{-5}}{10^{-2}} \approx 6{,}2 \cdot 10^{-3}\,\mathrm{mol/L}.$$

This alone would already correspond to $pH \approx -\log_{10}(6.2 \times 10^{-3}) \approx 2.21$.
Important: Real systems contain buffer/complexation mechanisms and transport that can strongly change the local pH dynamics. Nevertheless, the calculation shows why pH measurements and chemical analytics in Chapter 6 are central.

3.7 Minimal model for later chapters

For mechanistic cycles (Chapter 4) and energy balances (Chapter 5), it is helpful to write the cell as a system with a few **state variables**. A simple (lumped) model may contain the following quantities:

$$\mathbf{x} = \left[c_{\mathrm{Fe}^{3+}},\ c_{\mathrm{Fe}^{2+}},\ c_{\mathrm{H}^+},\ n_{\mathrm{H}_2},\ \theta_L\right]^\top \tag{3.6}$$

where θ_L (symbolically) describes the binding/complexation state of the polyol ligands. In addition, there are transport and relaxation times (diffusion, mixing) and a thermal model for $T(t)$ or the heat flow to the environment.

Outlook

In the next chapter, we formulate the **mechanistic cycle** from these building blocks: “closing the circuit → directed reaction → cooling → opening → mixing → thermally driven regeneration”. [8]

Chapter 4

The mechanistic TEC-G/TREC cycle

Learning objective of this chapter

We formulate the operation of a TEC-G/TREC cell as a **mechanistic cycle**:

- states (A–F) and the associated physicochemical processes,
- what happens when the circuit is **closed** vs. **opened**,
- why and when a cell **cools** and how to interpret **regeneration** thermodynamically,
- and which **measurement signatures** you would expect if the model is correct.

As a consistent case study we use the published Heiontec explanatory model. [8]

4.1 The cycle in one sentence

A TEC-G/TREC cell uses a **thermodynamically coupled** redox chemistry: *During discharge, electrical work is delivered while (partly) absorbing heat (⇒ cooling); in the open-circuit state the cell absorbs heat from the environment and restores its initial composition (⇒ regeneration).* [1,8]

4.2 States A–F: overview as a table

To describe the cycle reproducibly, we break it down into states. The states are **model-specific labels** (no universal standard), guided by the Heiontec six-step model. [8]

State	Switching state	Physicochemical description (short)
A	open	initial distribution of species; overall reaction blocked
B	closed	reaction is "enabled" via separated electrodes; current flow starts
C	closed	ion transport + pH gradient; Fe^{3+} complex reduction / H_2 oxidation proceed
D	closed → end	reactivity declines; cell cools; power drop
E	open	relaxation: diffusion/migration, pH equalization, mixing
F	open	thermally driven back-formation/complexation; approach to A

Table 4.1: State overview (A–F) as a guide for the mechanistic cycle.

4.3 Cycle graphic: A–F as a cyclic process

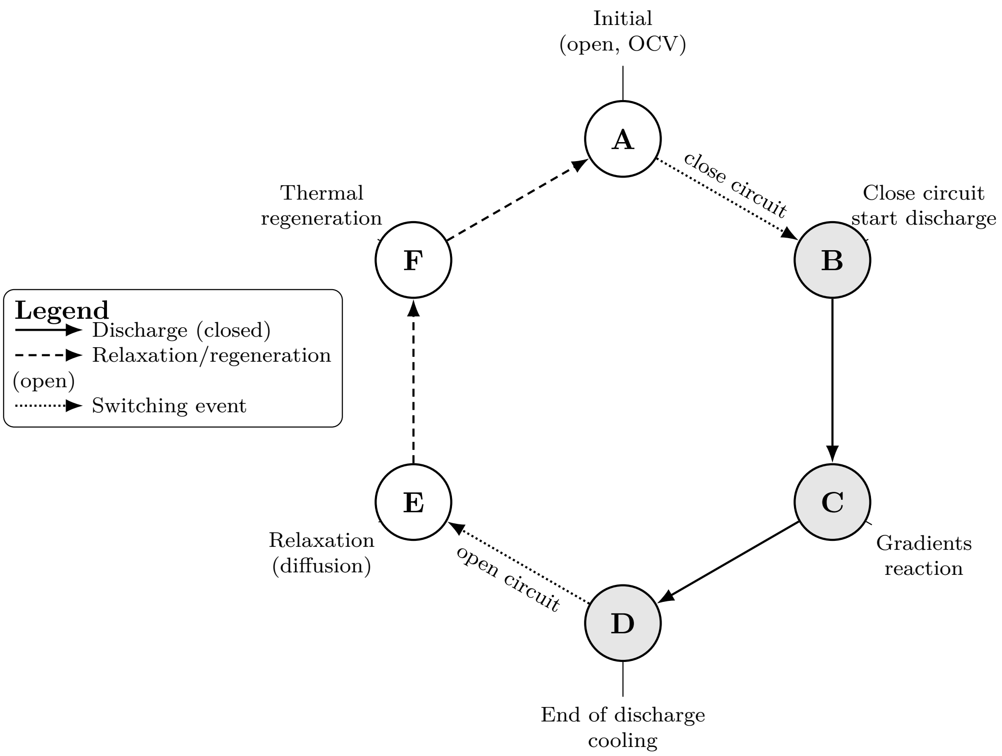

Figure 4.1: Cycle representation with clear phase separation: **Discharge** with the circuit closed (B–D, solid arrows) and **relaxation/regeneration** with the circuit open (E–A, dashed arrows). A–B and D–E mark the switching event. [8]

4.4 The two core half-reactions (as the "engine" of the cycle)

For the Heiontec model, the formal overall reaction (Chapter 3) [8]:

$$\mathrm{Fe}^{3+} + \frac{1}{2}\,\mathrm{H}_2 \longrightarrow \mathrm{Fe}^{2+} + \mathrm{H}^{+}. \tag{4.1}$$

In the discharge step it is realized by two spatially separated half-processes:

Anode (Fe electrode, only H_2/H^+)

$$\frac{1}{2}\,\mathrm{H}_2 \longrightarrow \mathrm{H}^{+} + \mathrm{e}^{-}. \tag{4.2}$$

Cathode (C electrode, only Fe^{3+}/Fe^{2+})

$$\mathrm{Fe}^{3+} + \mathrm{e}^{-} \longrightarrow \mathrm{Fe}^{2+} \quad \text{(possibly via complexes)}. \tag{4.3}$$

Key point: Why is it "blocked" at all?

The overall reaction (4.1) would also be thermodynamically possible without an external circuit. **Blocked** here means: the system is built (selectivity/passivation/complex chemistry) such that the reaction is strongly inhibited *kinetically or spatially* without an external circuit. Only when the circuit is closed are electrons made available via the load and the reaction "proceeds in an orderly way". [8]

4.5 Mechanistic description step by step

We now describe each state as a combination of:

1. **switching state** (open/closed),
2. **dominant chemistry** (which species changes where),
3. **transport** (ions, diffusion, mixing),
4. **thermal behavior** (heat uptake/release, cooling).

4.5.1 State A: initial state (open circuit)

In state A the circuit is open: no macroscopic electron current flows. The cell shows an **open-circuit voltage** (OCV), determined by the current activities of Fe^{3+}/Fe^{2+}, H^+/H_2, as well as complexation/solvation states (see the fundamentals in Chapter 2). [6]

Model assumption (Heiontec): Fe^{3+} is present largely as a polyol/ligand complex, and the electrodes react selectively, so that the overall reaction without an external electron path can proceed only to a limited extent. [8]

4.5.2 A → B: closing the circuit (start of discharge)

When the circuit is closed, an external electron path is provided. The half-processes (4.2) and (4.3) can then proceed simultaneously:

- at the Fe electrode, H_2 is oxidized, producing H^+,
- at the C electrode, Fe^{3+} is reduced,
- the electrons flow through the load from the Fe to the C electrode.

4.5.3 State B: "ordered" reaction, current flow established

In B, a characteristic start-up transient occurs: The double layer recharges, local concentration profiles form, and the terminal voltage drops from the open-circuit voltage to a load value. This can be observed in almost all electrochemical systems.

4.5.4 B → C: build-up of gradients (pH, redox, complexation state)

While current flows, gradients arise almost inevitably:

- near the Fe electrode, the local H^+ activity increases (pH decreases),
- near the C electrode, the Fe^{3+} activity decreases while Fe^{2+} increases,
- if Fe^{3+} is complexed, a "complex opening" during reduction can occur, which is described in the model as an entropy increase. [8]

Important consequence

Voltage and temperature traces are tightly coupled here: If activities (Nernst) and complexation states change, not only E changes, but often also $\partial E/\partial T$, i.e., the entropic signature.

4.5.5 State C: quasi-steady operation (transport-limited)

In C, quasi-steady discharge operation may be present: The reaction proceeds, but is increasingly limited by transport (diffusion/migration) and/or by depletion of reactive species in the boundary layer.

Typical indicators:

- voltage drops slowly (concentration polarization),
- temperature drifts (heat uptake vs. losses),
- current/voltage respond sensitively to mixing.

4.5.6 C → D: cooling and reaction stop (end of the discharge phase)

The Heiontec model reports that the cell cools during discharge and eventually “no reaction is possible anymore” until heat has been absorbed again. [8]

Thermodynamic interpretation. If the reversible heat contribution (entropic heat uptake) is larger than the irreversible losses, the net result is heat uptake and thus cooling. The key message is not “Thomson”, but **reaction entropy** and reversible electrode heat. [1,6]

State D as a practical definition

In measurement data, D is often recognized by the fact that under the same load

- $V(t)$ drops strongly (power collapse),
- $I(t)$ decreases for a resistive load,
- and/or $T(t)$ reaches a minimum.

So D is less “a chemical state” than an **operating point** at which a limitation becomes active.

4.5.7 D → E: opening the circuit (end of discharge, start of relaxation)

As soon as the circuit is opened:

- the electron flow stops,
- electrochemical gradients begin to decay,
- the terminal voltage typically jumps upward (returning toward the OCV).

4.5.8 State E: relaxation (diffusion, mixing, pH equalization)

In the open-circuit state, local gradients are reduced by transport processes: diffusion, migration (if a residual field remains), natural convection. In the Heiontec model it is described that H^+ and Fe^{2+} become evenly distributed again. [8]

Measurable signatures. E is typically associated with time-dependent recovery of voltage and temperature:

- $E_{\mathrm{OC}}(t)$ approaches a new equilibrium value,
- $T(t)$ approaches the ambient temperature again.

4.5.9 E → F: thermal feedback and chemical back-formation

The Heiontec model describes that in the open-circuit state, by absorbing ambient heat, the cell enters a state in which Fe^{3+} complexes and H_2 are rebuilt, until the initial state is reached. [8]

Important (scientific context). Such a back-formation must be consistent with the 2nd law: If the cell is back in its initial state after a cycle and has delivered net work, then this work must ultimately originate from an external non-equilibrium source (e.g., a heat flux/temperature lift). [1, 5]

4.5.10 State F: "ready" for the next discharge pulse

In F, the state variables (activities, complexation state, temperature) are again close to A. In practice, this is a matter of:

- time (relaxation time),
- heat transfer (how fast $T \to T_{\mathrm{amb}}$),
- and chemical kinetics (complexation/redox turnover).

4.6 Time traces: what do $I(t)$, $V(t)$ and $T(t)$ typically look like?

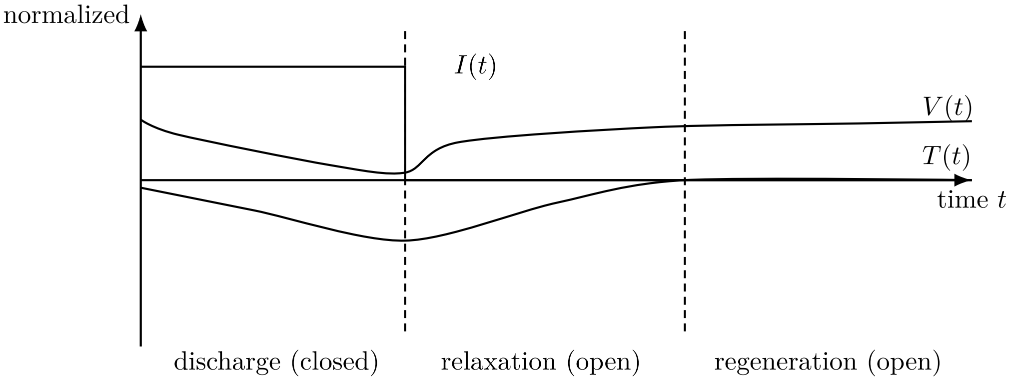

Figure 4.2: Schematic time traces of a cycle (qualitative): Under load, current flows and voltage drops; the cell cools. In the open-circuit state, voltage and temperature recover through relaxation and heat uptake.

4.7 Example calculations: work, heat and temperature change

4.7.1 Example 4.1: electrical work per discharge pulse

Example 4.1: energy from a load pulse

Assume a simple discharge pulse:

$$I = 20\,\mathrm{mA}, \qquad V \approx 0{,}50\,\mathrm{V}, \qquad t = 120\,\mathrm{s}.$$

Then the delivered electrical work (energy) is

$$W_{\mathrm{el}} \approx VIt = 0.50 \cdot 0.020 \cdot 120 \approx 1{,}2\,\mathrm{J}.$$

Interpretation: For small demonstrator cells, energy amounts in the joule range per cycle are readily plausible; whether this comes from ambient heat or from chemical consumption is decided by the balance.

4.7.2 Example 4.2: cooling from heat uptake (thermal capacity)

Example 4.2: How large can a temperature drop be?

Assume the effective thermal capacity of the cell (electrolyte + housing + electrodes) is

$$C_{\mathrm{th}} = 20\,\mathrm{J/K}.$$

If, during a discharge pulse, the cell must take up net

$$Q_{\mathrm{in}} = 1{,}0\,\mathrm{J}$$

heat (because the reversible contribution dominates), then approximately

$$\Delta T \approx \frac{Q_{\mathrm{in}}}{C_{\mathrm{th}}} = \frac{1.0}{20} = 0{,}05\,\mathrm{K}.$$

Interpretation: Noticeable temperature changes (several kelvin) require either very small C_{th}, large amounts of heat, strong thermal insulation, or local (not fully averaged) temperature peaks. Therefore, sensor placement in Chapter 6 is crucial.

4.7.3 Example 4.3: chemical conversion per cycle (consistency check)

With $Q = It$ and $n = 1$, the conversion of Fe^{3+} and H_2, respectively (see Chapter 3), is:

$$n_{\mathrm{Fe}^{3+}} = \frac{Q}{F}, \qquad n_{\mathrm{H}_2} = \frac{Q}{2F}.$$

For $I = 20\,\mathrm{mA}$ and $t = 120\,\mathrm{s}$, $Q = 2{,}4\,\mathrm{C}$ and thus

$$n_{\mathrm{Fe}^{3+}} \approx \frac{2.4}{96485} \approx 2{,}5 \cdot 10^{-5}\,\mathrm{mol}, \qquad n_{\mathrm{H}_2} \approx 1{,}2 \cdot 10^{-5}\,\mathrm{mol}.$$

Interpretation: Even small discharge pulses create measurable changes that can be checked analytically (Fe^{2+}/Fe^{3+}, pH, H_2 inventory). [10]

4.8 What should one observe experimentally if the cycle is correct?

Without anticipating the full measurement methods (Chapter 6), the cycle model allows concrete **predictions** to be derived:

1. **Correlation current ↔ cooling:** the temperature minimum should occur during the discharge phase and scale with the integrated current (charge), at least in a regime without strong side reactions.
2. **Relaxation signatures:** after load disconnect, $E_{\mathrm{OC}}(t)$ should show a time-dependent recovery (decay of gradients).
3. **Chemical balanceability:** $\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}$ and pH should change according to Faraday stoichiometry — or deviations must be explained by side reactions.
4. **Heat/energy balance:** over many cycles it must hold that net work cannot arise without a net heat flux/temperature lift or material consumption. An isothermal test is therefore particularly informative. [1, 5]

Pragmatic note

If a cycle looks "too good" (lots of electrical energy, hardly any measurable heat flux, hardly any chemical turnover), this is a **warning sign**: either measurement pathways are missing (artifacts), or there exists an unrecognized energy source (e.g., side reactions, gas/moisture exchange, corrosion).

4.9 Brief conclusion

Take-aways

1. The cycle can be described as the sequence A–F: **discharge** (closed) and **relaxation/regeneration** (open).
2. The driving chemistry is (model-wise) $\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}$ coupled to $\mathrm{H}_2/\mathrm{H}^+$, spatially separated by electrode selectivity. [8]
3. Cooling is thermodynamically plausible via **entropic, reversible heat uptake** — not primarily via the Thomson effect.
4. The cycle makes testable predictions: $I(t)$, $V(t)$, $T(t)$, and the chemical balance must be consistent.

Chapter 5

Energy balances, efficiencies and limits

Learning objective of this chapter

In this chapter we build the **tool set** to *rigorously* check statements about TEC-G/TREC cells:

- **energy and entropy balances** for discharge, regeneration, and cyclic operation,
- meaningful definitions of **efficiency** and **power density**,
- thermodynamic **limits** (2nd law, Carnot/exergy),
- as well as simple **back-of-the-envelope estimates** that show which heat flows are required for observed powers.

The goal is not "calculating for the sake of calculating", but a **framework for checking** that makes measurements (Chapter 6) interpretable. [1, 2, 5]

5.1 What has to go into a balance? (System boundaries)

Before writing equations, one has to clearly state **what** the system is. For a cell, there are two common system boundaries:

1. **Cell as a closed system:** electrolyte, electrodes, housing, internal gas phase. There is *no* mass exchange with the outside (no gases, no liquids). Energy can cross the boundary as heat and electrical work.
2. **Cell as an open system:** if, for example, gas escapes to the outside, water evaporates, or reactants are supplied from outside, there is additionally a **chemical energy flow** via mass flows.

Why this matters

Many seemingly "surprising" results disappear as soon as one realizes that the system was in fact open (e. g. H_2 leakage, O_2 ingress, humidity changes), or that electrodes change irreversibly (corrosion, side reactions).

In the Heiontec explanatory model, a **closed** vessel is described. [8] Therefore, the closed-balance case is a central test assumption.

5.2 First law for discharge: $\Delta H = Q - W_{\mathrm{el}}$

We consider a discharge reaction at constant pressure. Then, for the cell (closed system, no shaft work) we have:

$$\Delta H = Q - W_{\mathrm{el,out}}, \tag{5.1}$$

where

- Q is the **heat** that flows *into the cell* (positive: heat uptake),
- $W_{\mathrm{el,out}}$ is the **electrical work** that the cell *delivers to the outside* (positive during discharge).

From (5.1) it follows:

$$Q = \Delta H + W_{\mathrm{el,out}}. \tag{5.2}$$

5.2.1 Reversible limiting case

In the reversible case, $W_{\mathrm{el,out,rev}} = -\Delta G$ (Chapter 2) [5,6] and thus:

$$Q_{\mathrm{rev}} = \Delta H - \Delta G = T\Delta S. \tag{5.3}$$

This is the central point for TEC-G/TREC: if $\Delta S > 0$, then $Q_{\mathrm{rev}} > 0$, the cell must absorb heat, and can therefore **cool** if the heat replenishment is limited.

5.3 Reversible vs. irreversible: heat uptake, heat rejection, losses

In real cells, during discharge we typically have $V < E_{\mathrm{rev}}$. The difference arises from

- activation overpotential,
- concentration/transport overpotential,
- ohmic losses (I^2R).

5.3.1 Bernardi equation (practical heat formula)

A very common heat-balance form in battery technology is the so-called **Bernardi equation**. [6,12] With our sign conventions (discharge: $I > 0$, heat released to the environment positive) it reads:

$$\dot{Q}_{\mathrm{gen}} = I\,(E_{\mathrm{rev}} - V) - I\,T\left(\frac{\partial E_{\mathrm{rev}}}{\partial T}\right), \tag{5.4}$$

where $\dot{Q}_{\mathrm{gen}}$ is the **heat rate** that net *goes to the environment as heat* (positive: heating, negative: cooling).

Interpretation.

- $I(E_{\mathrm{rev}} - V)$ is **irreversible** (dissipation): it is always converted into heat.
- The term $-I\,T(\partial E_{\mathrm{rev}}/\partial T)$ is **reversible-entropic**: it can be positive or negative and is the key to thermo-electrochemical effects.

If $\dot{Q}_{\mathrm{gen}} < 0$, the cell cools net (it absorbs heat from the environment).

Bridge to Chapter 2: same physics, different notation

Chapter 2 considered the net heat flow $\dot{Q}_{\mathrm{env}\to\mathrm{cell}}$. Both representations are equivalent:

$$\dot{Q}_{\mathrm{env}\to\mathrm{cell}} = -\dot{Q}_{\mathrm{gen}} = I\,T\left(\frac{\partial E_{\mathrm{rev}}}{\partial T}\right) - I(E_{\mathrm{rev}} - V).$$

5.3.2 Example 5.1: Cooling or heating?

Example 5.1: Estimate $\dot{Q}_{\text{gen}}$ from measured quantities

Assume that at 25 °C one measures:

$$I = 50\,\text{mA}, \quad E_{\text{rev}} = 0{,}80\,\text{V}, \quad V = 0{,}65\,\text{V}, \quad \frac{\partial E_{\text{rev}}}{\partial T} = 1{,}0\,\text{mV/K}.$$

Then:

$$I(E_{\text{rev}} - V) = 0.05 \cdot (0.15) = 7{,}5\,\text{mW},$$

$$IT\frac{\partial E}{\partial T} = 0.05 \cdot 298 \cdot 0.001 \approx 14{,}9\,\text{mW}.$$

Thus:

$$\dot{Q}_{\text{gen}} \approx 7.5 - 14.9 = -7{,}4\,\text{mW}.$$

Result: The cell cools net by about 7 mW (provided heat transfer allows it).

5.4 Second law: why a cyclic process cannot be “free”

The second law in Clausius form reads:

$$\oint \frac{\delta Q}{T} \leq 0. \tag{5.5}$$

For a **cyclic** process (the cell returns to its initial state) this means: one cannot arbitrarily convert heat from *one* heat reservoir into work.

5.4.1 Kelvin-Planck statement (everyday)

A heat engine that interacts with **only** a single heat reservoir cannot, in one cycle, deliver only work to the outside. There must be at least a second temperature level or another non-equilibrium source. [5]

Consequence for TEC-G/TREC

If a cell delivers net electrical energy cyclically, then at least one of the following quantities must play an *external* role in the balance:

- a **heat flow between two effective temperatures** (classically: T_{hot} and T_{cold}),
- or a **mass flow/chemical consumption** (e. g. side reactions),
- or another external non-equilibrium source (radiation, humidity, pressure, etc.).

The measurement methods in Chapter 6 are chosen such that these possibilities can be separated from one another.

5.5 Efficiencies: which definition is meaningful?

There is not “the” efficiency, but several meaningful definitions, depending on whether operation is **gradient-driven** (thermogalvanic) or **cyclic** (TREC).

5.5.1 Gradient operation (stationary, thermogalvanic/TEC-G)

If a cell is operated between a hot and a cold end, a typical definition is:

$$\eta_{\text{th}} = \frac{P_{\text{el}}}{\dot{Q}_{\text{in}}}, \tag{5.6}$$

where $\dot{Q}_{\text{in}}$ is the heat flow that enters the cell at the hot end. In practice, $\dot{Q}_{\text{in}}$ is difficult to determine because heat also flows **parasitically** through heat conduction in the housing or via electrodes/leads. [2]

5.5.2 Cyclic operation (TREC)

For a cycle, the natural definition is:

$$\eta_{\text{cycle}} = \frac{W_{\text{el,net}}}{Q_{\text{in,cycle}}}, \tag{5.7}$$

where $Q_{\text{in,cycle}}$ is the amount of heat that has to enter the cycle *at a high temperature level* (typically in a heating step).

5.5.3 Exergy efficiency (2nd-law efficiency)

If the heat source is close to ambient temperature, exergy is particularly informative. For an amount of heat Q from a source at T into an environment at T_0, the exergy is

$$B_Q = Q\left(1 - \frac{T_0}{T}\right). \tag{5.8}$$

Thus:

$$\eta_{\text{ex}} = \frac{W_{\text{el,net}}}{B_{Q,\text{in}}}. \tag{5.9}$$

Why exergy is small when ΔT is small

At small temperature differences, $1 - T_0/T \approx \Delta T/T$ is small. That means: even large heat flows contain only little “useful” work.

5.6 Carnot limit and the order of magnitude of heat flows

For an ideal heat engine between T_{hot} and T_{cold} we have:

$$\eta_{\text{Carnot}} = 1 - \frac{T_{\text{cold}}}{T_{\text{hot}}}. \tag{5.10}$$

5.6.1 Example 5.2: Minimum heat flow for an observed power

Example 5.2: 10 mW from $\Delta T = 5\,\text{K}$

Let $T_{\text{hot}} = 300\,\text{K}$, $T_{\text{cold}} = 295\,\text{K} \Rightarrow \eta_{\text{Carnot}} \approx 1{,}7\,\%$. To generate an electrical power of $P_{\text{el}} = 10\,\text{mW}$, the heat flow would have to be at least:

$$\dot{Q}_{\text{in}} \geq \frac{P_{\text{el}}}{\eta_{\text{Carnot}}} \approx \frac{0.010}{0.0167} \approx 0{,}60\,\text{W}.$$

Interpretation: At very small ΔT, $\dot{Q}$ in the watt range quickly becomes plausible, even if the electrical power is only in the mW range.

5.7 Thermal bottlenecks: thermal resistance and time constant

An extremely practical parameter is the effective thermal resistance R_{th} between the cell and the environment:

$$\dot{Q} \approx \frac{\Delta T}{R_{\text{th}}}. \tag{5.11}$$

The associated thermal time constant is

$$\tau = R_{\text{th}} C_{\text{th}}, \tag{5.12}$$

where C_{th} is the thermal capacity of the cell.

5.7.1 Example 5.3: Upper bound on power from heat transfer

Example 5.3: $\Delta T = 3\,\text{K}$, $R_{\text{th}} = 5\,\text{K/W}$

From (5.11) it follows:

$$\dot{Q}_{\text{max}} \approx \frac{3}{5} = 0{,}6\,\text{W}.$$

At $\eta = 1\,\%$ this would be at most

$$P_{\text{el,max}} \approx \eta\,\dot{Q}_{\text{max}} = 6\,\text{mW}.$$

Interpretation: Even if the electrochemistry would “play along”, **thermal constraints** can limit the power.

5.8 Electrical bottlenecks: internal resistance and maximum power

In addition to the thermal side, the electrical side also limits the power. For a simple Thevenin approximation with open-circuit voltage E_{OC} and internal resistance R_{int} we have:

$$P(R_L) = \frac{E_{\text{OC}}^2\, R_L}{(R_{\text{int}} + R_L)^2}. \tag{5.13}$$

The maximum occurs at $R_L = R_{\text{int}}$:

$$P_{\text{max}} = \frac{E_{\text{OC}}^2}{4R_{\text{int}}}. \tag{5.14}$$

5.8.1 Example 5.4: Maximum power from E_{OC} and R_{int}

Example 5.4: 0,8 V and 20 Ω

With $E_{\text{OC}} = 0{,}8\,\text{V}$ and $R_{\text{int}} = 20\,\Omega$:

$$P_{\text{max}} = \frac{0.8^2}{4 \cdot 20} = \frac{0.64}{80} \approx 8\,\text{mW}.$$

Interpretation: Electrical and thermal limits must be satisfied simultaneously.

5.9 Energy flow diagram (Sankey-like, qualitative)

5.10 Context: What does this mean for the Heiontec cell?

The Heiontec explanatory model describes:

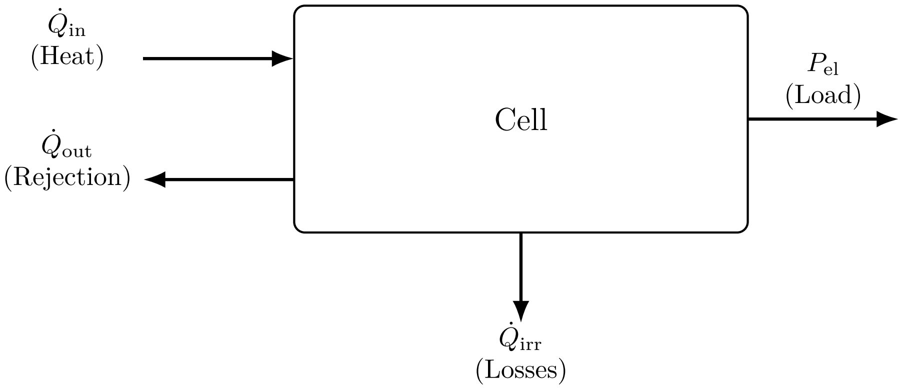

Figure 5.1: Qualitative energy-flow diagram: electrical power P_{el} arises from a combination of reversible heat uptake/rejection and irreversible losses. Whether the cell cools or heats is determined by the balance (5.4).

- a discharge phase with current delivery and cooling,
- followed by regeneration in the open state by absorbing ambient heat. [8]

Physical key message of this chapter. If such a cell delivers **net work** over many cycles and returns to the initial state, then the overall balance must clearly reveal:

1. **where** heat flows into the process (temperature level, heat flow),
2. **where** heat is rejected again (a second temperature level or other coupling),
3. and whether, in addition, **chemical consumption** (side reactions, corrosion, organic oxidation) occurs.

This is exactly why, in Chapter 6, calorimetry and chemical analytics are not “nice-to-haves”, but mandatory if one wants to make TEC-G/TREC claims scientifically robust.

5.11 Short conclusion

Take-aways

1. For discharge: $Q = \Delta H + W_{\text{el,out}}$; in the reversible case $Q_{\text{rev}} = T\Delta S$.
2. The real heat rate is described by (5.4): losses heat up, entropic contributions can cool.
3. The 2nd law enforces: net work in a cyclic process requires at least two effective temperature levels or an external chemical/material flow.
4. Power is often limited by **thermals** (R_{th}, τ) and **electrics** (R_{int}, P_{max}).

Chapter 6

Measurement methods, validation and typical artifacts

Learning objectives of this chapter

This chapter turns “exciting curves” into robust science. We show how to measure TEC-G/TREC cells in such a way that you end up with a clear answer to the question: *Where does the energy come from?*

- **Electrical:** $E(t)$, $I(t)$, $P(t)$, internal resistance, impedance.
- **Thermal:** $T(t)$, heat flow, heat transfer, calorimetric energy balance.
- **Chemical:** Fe^{2+}/Fe^{3+}, pH, H_2 inventory, organic by-products.
- **Validation:** controls, system boundaries, uncertainty, typical misinterpretations.

Many of these methods are standard in electrochemistry and battery research. [6, 7, 13]

6.1 Measurement philosophy: three balances or it was not science

A TEC-G/TREC cell is a **coupled** system of chemistry, electricity, and thermal physics. If you measure only voltage and current, it is easy to draw the wrong conclusions. For a defensible conclusion you need at least:

1. **Electrical balance:** $W_{\mathrm{el}} = \int V I \, dt$,
2. **Thermal balance:** heat flow / calorimetry (cf. Bernardi equation, Chapter 5) [12],
3. **Chemical balance:** matching Faradaic conversion with analytics (Fe, pH, H_2, by-products).

Golden rule

If a measurement campaign does not tell whether the system was fed **chemically**, **thermally**, or by **artifacts**, then at its core it was a demonstration — not a validation.

6.2 Electrical measurements

6.2.1 Basic equipment and wiring

For reproducible measurements, the game changer is often not “better cells” but “better cables”.

Recommendations.

- **4-wire (Kelvin) measurement** for voltage when currents are in the mA range or higher.
- Measure current using a **shunt** (calibrated) or a precision ammeter.
- Consistent reference points (star ground), avoidance of ground loops.
- Minimize temperature gradients along leads (Seebeck artifacts).

6.2.2 Open-circuit voltage $E_{\mathrm{OC}}(t)$ and drift

Open-circuit measurements are important because they capture the thermodynamic **EMF** (Chapter 2). But: E_{OC} often drifts because:

- concentration profiles relax,
- the gas phase/electrolyte relax,
- electrode surfaces reorganize,
- temperature is not stable.

Practical tip: how to measure $E_{\mathrm{OC}}(T)$ cleanly

1. Place the cell in a temperature-stable environment (thermostat/temperature-controlled bath).
2. After each temperature step, wait long enough: τ from a thermal time-constant model (Chapter 5).
3. Only record E_{OC} when $|dE/dt|$ and $|dT/dt|$ are below defined thresholds.

6.2.3 I–V characteristics and maximum power

An I–V curve is quick to measure, but easy to misinterpret. For TEC-G/TREC cells, it is important to note:

- The curve is often **time-dependent** (chemistry/temperature changes during the measurement).
- Therefore better: a **stepwise load schedule** with fixed hold intervals and logging of $V(t)$, $I(t)$, $T(t)$.
- A true $P_{\max}$ requires the cell to be **quasi-stationary** in that state.

6.2.4 Pulse and relaxation measurements

A very powerful experiment:

1. short load pulse (1 s to 60 s),
2. then open circuit and observe the voltage return $E_{\mathrm{OC}}(t)$.

Interpretation (rough):

- fast recovery (ms–s): double layer, ohmic,
- intermediate times (s–min): concentration polarization, diffusion,
- long times (min–h): chemical back-reaction, complexation, gas equilibrium.

6.2.5 Impedance spectroscopy (EIS)

EIS separates processes by time scales. You measure the complex impedance $Z(\omega)$ as a function of frequency:

$$Z(\omega) = \frac{\tilde{V}(\omega)}{\tilde{I}(\omega)}.$$

Typical assignment (simplified) [7, 13]:

- high f: ohmic electrolyte/contact resistance R_Ω,
- medium f: charge-transfer resistance R_{ct} and double-layer capacitance C_{dl},
- low f: diffusion (Warburg), mass transport, chemical relaxation.

Important: EIS is not a "push-button" tool

EIS is extremely informative, but only if:

- the system is **stationary** during the measurement,
- the excitation signal is small enough (linearity),
- and suitable equivalent circuits/models are used.

For TEC-G/TREC cells, EIS is particularly interesting to see whether an observed energy output is more likely due to **capacitive effects** or **faradaic reactions**.

6.3 Electrical evaluation: power and energy from measurement data

6.3.1 Discrete integration

Measuring instruments provide discrete samples V_k, I_k with time intervals Δt_k. The electrical energy is then:

$$W_{\text{el}} \approx \sum_{k=1}^{N} V_k I_k \, \Delta t_k. \tag{6.1}$$

Example 6.1: Energy from a log file

Assume that $N = 600$ samples were logged with $\Delta t = 1\,\text{s}$. If, on average, $V = 0{,}55\,\text{V}$ and $I = 12\,\text{mA}$ are present, then:

$$W \approx V I N \Delta t = 0.55 \cdot 0.012 \cdot 600 \approx 3{,}96\,\text{J}.$$

Remember: This is the basis of any energy balance — without this number, discussions about "efficiency" are meaningless.

6.4 Thermal measurements

6.4.1 Sensors: what are you actually measuring?

Temperature measurement is tricky because cells can be spatially inhomogeneous. Key points:

- Sensor position: surface vs. electrolyte vs. electrode terminal.
- Thermal contact: bonding/pressing, thermal paste, insulation errors.
- Sensor inertia: the sensor time constant can smear out dynamics.

6.4.2 Thermal calibration: R_{th} and C_{th}

A very useful minimal model is a first-order system:

$$C_{\text{th}}\frac{dT}{dt} = \dot{Q}_{\text{in}}(t) - \frac{T - T_{\text{amb}}}{R_{\text{th}}}.$$

At open circuit ($\dot{Q}_{\text{in}} = 0$) you obtain an exponential approach:

$$T(t) - T_{\text{amb}} = (T_0 - T_{\text{amb}})e^{-t/\tau}, \quad \tau = R_{\text{th}}C_{\text{th}}.$$

Example 6.2: Determining τ from a decay curve

If $T(t) - T_{\text{amb}}$ has fallen to $1/e$ of its initial value after $120\,\text{s}$, then $\tau \approx 120\,\text{s}$. With a known C_{th}, you can determine R_{th} — or vice versa.

6.4.3 Calorimetry

For a defensible statement, **isothermal calorimetry** is ideal: You keep the cell temperature constant and measure the heat flow required to maintain isothermality. Then the heat balance is direct.

In combination with the Bernardi equation [12], you can check:

- does the entropic heat agree with $\partial E/\partial T$?
- are losses consistent with $E_{\text{rev}} - V$?
- are there additional heat sources (side reactions)?

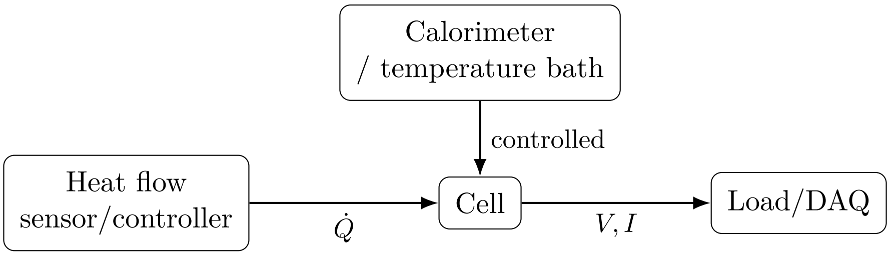

Figure 6.1: Principle of a calorimetric measurement: heat flow $\dot{Q}$ and the electrical quantities V, I are recorded simultaneously.

6.5 Chemical analytics

6.5.1 Fe^{2+}/Fe^{3+}: spectrophotometry (Ferrozine/phenanthroline)

Fe^{2+} can be determined very sensitively by photometry in aqueous samples, e. g. with **Ferrozine** (complex with strong absorption). [14] For Fe^{3+}, you either determine it:

- directly (if a suitable method/complexation is available), or
- **total iron** after reduction of $Fe^{3+} \to Fe^{2+}$ and taking the difference.

Example 6.3: Faradaic conversion vs. analytics

If $Q = 6\,\text{C}$ were transferred during the discharge pulse, the theoretical conversion is $\Delta n_{\text{Fe}^{3+}} = Q/F \approx 6{,}2 \cdot 10^{-5}\,\text{mol}$ (Chapter 3). With a volume sample of $V = 10\,\text{mL}$, this corresponds to $\Delta c \approx 6{,}2 \cdot 10^{-3}\,\text{mol/L}$. Photometry should see this order of magnitude — otherwise either the model is wrong, or side reactions/complexation effects are distorting the measurement.

6.5.2 pH and proton balance

In such cells, pH is **not only** a "side parameter", but part of the stoichiometry (H^+ appears/disappears, cf. Chapter 3). Practical notes:

- pH electrodes can drift at high ionic strength / in the presence of organic components.
- Enable temperature compensation and document **calibration** before/after the measurement series.
- Best: interpret pH as a **trend** and in combination with Fe analytics.

6.5.3 H_2 inventory: pressure, volume, GC

If the cell is closed, you can determine H_2 indirectly via pressure changes. Using the ideal-gas approximation:

$$n_{\text{gas}} = \frac{pV}{RT}. \tag{6.2}$$

Example 6.4: H_2 from a pressure increase (closed vessel)

Assume a gas phase with $V = 50\,\text{mL}$ increases by $\Delta p = 20\,\text{mbar}$ at $T = 298\,\text{K}$. Then:

$$\Delta n = \frac{\Delta p\, V}{RT} = \frac{2000 \cdot 50 \times 10^{-6}}{8.314 \cdot 298} \approx 4{,}0 \cdot 10^{-5}\,\text{mol}.$$

This corresponds to an H_2 volume of about $1\,\text{mL}$ (at 1 bar, RT).

For high accuracy: gas chromatography (GC) or mass spectrometry.

6.5.4 Organic components: what happens to the polyols?

If polyols are "set to be reducing", you must check whether they remain chemically stable over cycles or oxidize. Suitable methods:

- HPLC (separation/quantification),
- NMR (structure),
- GC-MS (volatile/derivatized products).

This is particularly important to distinguish **chemical energy consumption** from **harvesting thermal energy**.

6.6 Control and validation experiments (checklist)

6.6.1 Minimum set of controls

1. **Dummy cell**: a purely ohmic resistor of the same form factor in the same measurement setup (checks thermoelectricity of the wiring and DAQ artifacts).
2. **Blank electrolyte**: without Fe redox (checks capacitance/electrode artifacts).
3. **Isothermal operation**: cell in bath/calorimeter, $\Delta T \approx 0$ (checks whether net energy arises without a temperature swing).
4. **Gas-tight vs. intentionally vented**: checks the role of the H_2 inventory and mass exchange.
5. **O_2 influence**: measurement in air vs. inert (N_2/Ar), because oxygen can affect redox chemistry.

6.6.2 Measurement protocol (minimal, but robust)

Protocol template (minimal)

1. **Cell ID**, build, electrolyte volume, electrode areas, sensor serial numbers.
2. **Initial state**: T, pH, $\mathrm{Fe}^{2+}/\mathrm{Fe}^{3+}$, gas pressure, OCV.
3. **Load profile**: defined (resistance/CC/CP), duration, sampling rate.
4. **Logging**: $V(t)$, $I(t)$, $T(t)$ (multiple positions), if applicable $\dot{Q}(t)$, gas pressure.
5. **Final state**: pH again, Fe analytics, gas pressure, visual inspection of the electrodes.
6. **Balance**: W_{el} from (6.1), chemical conversions, heat (if available).

6.7 Typical artifacts and how to uncover them

6.7.1 Pseudocapacitance and the double layer as an “energy source”

Many cells can deliver energy for a short time because:

- the double layer is charged,
- adsorbed species rearrange,
- surface redox takes place in very small amounts.

This can look “battery-like”, but it is often **not cyclically regenerative**. Pulse and relaxation measurements as well as EIS help to separate these effects. [13]

6.7.2 Thermoelectric voltages in leads

If sensor leads see temperature gradients, a parasitic thermovoltage is generated (Seebeck effect) in the μV–mV range. For TEC-G/TREC cells (where mV matter), this can be fatal.

Countermeasures:

- symmetric wiring, isothermal terminals,
- same metals / minimized thermocouples,
- dummy cell as a control.

6.7.3 Leakage currents and instrument inputs

With high internal resistances, even DMM input currents or moist insulators can create leakage paths.

Countermeasures:

- document input impedance, use an electrometer if necessary,
- keep insulation dry, guarding,
- measurement against short-circuit/open-circuit control.

6.7.4 Chemical artifacts: corrosion and side reactions

If electrodes corrode or organic additives are oxidized, that provides real energy, but not from “ambient heat”. That is exactly why chemical balancing is needed (Fe analytics, organic analytics, electrode inspection).

6.8 Uncertainty and error propagation (short, but useful)

A result without uncertainty is hard to interpret. For products like $P = VI$, a rough (uncorrelated) error propagation is:

$$\left(\frac{\sigma_P}{P}\right)^2 \approx \left(\frac{\sigma_V}{V}\right)^2 + \left(\frac{\sigma_I}{I}\right)^2 .$$

For the energy integration (6.1), additional sampling and drift errors apply. As a starting point, literature on error analysis is helpful. [15]

6.9 Brief conclusion

Take-aways

1. Without an **electrical + thermal + chemical** balance, TEC-G/TREC is not valid.
2. 4-wire measurement, defined load profiles, and clean integration are mandatory.
3. Calorimetry + the Bernardi equation provide a direct test for “cools/heats” and for side reactions.
4. Fe analytics (e. g. Ferrozine) and H_2 monitoring link measurement data to stoichiometry.
5. Artifacts (thermovoltages, capacitance, leakage currents) are common and must be actively ruled out.

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