FUEL CELL CHARACTERIZATION

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WHAT DO WE WANT TO CHARACTERIZE?

- **Overall performance** (i-V curve, power density)
- **Kinetic properties** ($\eta_{\text{act}}$, $j$, $\alpha$, electrochemically active surface area)
- **Ohmic properties** ($R_{\text{ohmic}}$, electrolyte conductivity, contact, electrode, interconnect resistances)
- **Mass transport properties** ($j_L$, $D_{\text{eff}}$, pressure losses, reactant/product homogeneity)
- **Parasitic losses** ($j_{\text{leak}}$, side reactions, fuel crossover)
- **Electrode structure** (porosity, tortuosity, conductivity)
- **Catalyst structure** (thickness, porosity, catalyst loading, particle size, electrochemically active surface area, catalyst utilization, triple-phase boundaries)
What do we want to characterize?

- Flow structure (pressure drop, gas distribution, conductivity);
- Heat generation/heat balance;
- Lifetime issues (lifetime testing, degradation, cycling, startup/shutdown, failure, corrosion, fatigue).
OVERVIEW OF CHARACTERIZATION TECHNIQUES

Two types of characterization techniques:

- **Electrochemical Characterization Techniques (In Situ):** the electrochemical variables are voltage, current, time. Characterization of the performances of fuel cell devices under operating conditions.

- **Ex Situ Characterization Techniques:** for the detailed structure and properties of the individual components.
OVERVIEW OF CHARACTERIZATION TECHNIQUES

- IN SITU TECHNIQUES

1. **Current – Voltage (j-V) measurement**: quantitative evaluation of fuel cell performance and power density.

2. **Current Interrupt Measurement**: Ohmic and nonohmic processes. Only useful for high-power fuel cell systems.

3. **Electrochemical Impedance Spectroscopy (EIS)**: can distinguish between ohmic, activation, and concentration losses.

4. **Cyclic voltammetry (CV)**: provides insight into fuel cell reaction kinetics.
OVERVIEW OF CHARACTERIZATION TECHNIQUES

EX SITU TECHNIQUES

1. Porosity determination: most of the techniques are destructive tests.


3. Gas permeability: for the understanding mass transport in fuel cell electrodes. Gas permeability testing of electrolytes is critical to the development of ultrathin membranes.

4. Structure Determinations: microscopy, diffraction techniques. Critical information when new catalysts, electrodes, or electrolytes are being developed or when new processing methods are used.

5. Chemical Determinations.
Fundamental Electrochemical Variables: Voltage, Current and Time.

Interdependence between current and voltage: only two fundamental types of electrochemical characterization techniques: Potentiostatic and galvanostatic techniques.

- **Potentiostatic Techniques:** The voltage of a system is controlled by the user and the resulting current is measured.
- **Galvanostatic Techniques:** The current of a system is controlled by the user and the resulting voltage response is measured.

For short time periods or under non-steady-state conditions, potentiostatic and galvanostatic measurements may deviate from one another. A system has not had enough time to relax to its steady-state condition.
Deviations from the steady state due to slow relaxation processes can be exploited to help to understand fuel cell behaviour.

- **Steady-State j-V Measurement**: The current (or the voltage) of the fuel cell is held fixed in time and the steady-state value of the voltage (or the current) is recorded after a long equilibrium time.

- **Current Interrupt Measurement**: A current is abruptly imposed at time $t=0$ and the system voltage resulting time-dependent approach to steady-state value is measured.

- **Cyclic Voltammetry**: The voltage applied to the system is swept linearly with time back and forth across a voltage window of interest. The resulting cyclic current is measured as a function of time and plotted as a function of the cyclic voltage.
**IN SITU ELECTROCHEMICAL CHARACTERIZATION**

- **Electrochemical Impedance Spectroscopy**: a sinusoïdal perturbation (usually a voltage perturbation) is applied to a system. The amplitude and phase shift of the resulting current response are measured. Measurements can be conducted over a wide range of frequencies, resulting in the construction of an impedance spectrum.
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BASIC FUEL CELL TEST STATION REQUIREMENTS

Electrochemical measurement equipment:
A potentiostat/galvanostat and a impedance analyser.
The voltage output of a fuel cell for a given density loading.

**High performances:** less loss and a higher voltage for a current density loading.
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- CURRENT-VOLTAGE MEASUREMENT

The steady state must be ensured.

The larger the fuel cell, the slower the approach to steady state.

Not unusual: 30 min to reach the steady state for a large automotive or residential fuel cell stack.

Current-voltage curve measurements are used to quantitatively describe overall performance of a fuel cell system.

At low current densities = the ohmic loss is usually small compared to the activation loss (approximation of the activation loss).
EIS = the most widely used technique for distinguishing the different losses.

Impedance = measure of the ability of a system to impede the flow of electrical current.

Impedance $Z = \frac{V(t)}{i(t)}$
IN SITU ELECTROCHEMICAL CHARACTERIZATION

- ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)

Impedance measurements are made by applying a small sinusoidal voltage perturbation and monitoring the system’s resultant current.

\[ V = V_0 \sin \omega t \quad \omega = 2\pi f \]

\[ i = i_0 \sin (\omega t - \varphi) \]
**ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)**

- Complex impedance:

\[
Z = Z_{\text{Re}} + Z_{\text{Im}} = \frac{\Delta E}{\Delta I}
\]

- In the complex representation, \( Z \) is given by a vector:

\[
|Z| = \sqrt{Z_{\text{Re}}^2 + Z_{\text{Im}}^2}
\]

\[
\varphi = \tan^{-1}\left(\frac{Z_{\text{Im}}}{Z_{\text{Re}}}\right)
\]
System linearity is required for impedance analysis.
- In a linear system, doubling the current will double the voltage.
- Electrochemical systems are not linear (ex: Butler Volmer equation).
- Using a small-signal voltage perturbation allows to circumvent this problem.
- In practice: a 1-20 mV AC signal is applied to the cell.
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- ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)
IN SITU ELECTROCHEMICAL CHARACTERIZATION

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)

Equivalent circuit models.

The processes that occur inside a fuel cell can be modelled using circuit elements.

Resistors and capacitors are used to describe the behaviour of electrochemical reaction kinetics, ohmic conduction processes and even mass transport.

Ohmic Resistance: the equivalent circuit representation of an ohmic conduction process is a simple resistor.

\[ Z_\Omega = R_\Omega \]

For a simple resistance: the imaginary component of impedance is zero, \( \varphi \) is zero and the impedance does not change with frequency.
IN SITU ELECTROCHEMICAL CHARACTERIZATION

- ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)

Equivalent circuit models.

Ohmic Resistance:

For a simple resistance: the imaginary component of impedance is zero, φ is zero and the impedance does not change with frequency.
IN SITU ELECTROCHEMICAL CHARACTERIZATION

- ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)

**Equivalent circuit models.**

**Electrochemical Reaction**: the impedance behaviour of the reaction interface can be modelled as a parallel combination of a resistor ($R_f$) and a capacitor ($C_{dl}$).

$R_f = \text{Faradaic Resistance}$

$C_{dl} = \text{Double-layer capacitance due to the separation of charge occurring across the reaction interface.}$

For a perfectly smooth electrode-electrolyte interface, $C_{dl}$ is typically on the order of 30 $\mu$F/cm$^2$.

With high-surface area fuel cell electrodes, $C_{dl}$ can be orders of magnitude larger.

The impedance response of a capacitor is purely imaginary.
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- ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)

Equivalent circuit models.

Electrochemical Reaction:

![Diagram showing electrochemical reaction and equivalent circuit models.](image)
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- ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)

Equivalent circuit models.

The equation relating voltage and current for a capacitor is:

\[ i = C \frac{dV}{dt} \]

For a sinusoidal voltage perturbation: \( V = V_0 e^{j\omega t} \)

\[ i(t) = C \frac{d(V_0 e^{j\omega t})}{dt} = C (j\omega)V_0 e^{j\omega t} \]

\[ Z = \frac{V(t)}{i(t)} = \frac{V_0 e^{j\omega t}}{C (j\omega)V_0 e^{j\omega t}} = \frac{1}{j\omega C} \]
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- ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)

Equivalent circuit models.

If a capacitor is placed in series with a resistor:

\[ Z_{\text{series}} = Z_1 + Z_2 \]

\[ Z = R + \frac{1}{j\omega C} \]
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- ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)

**Equivalent circuit models.**

**Electrochemical Reaction**: The capacitor and the resistor are in parallel rather than in series.

The reaction can be modelled by $R_f$ (Tafel simplification)

$$\eta_{act} = -\frac{RT}{\alpha n F} \ln i_0 + \frac{RT}{\alpha n F} \ln i$$

For a small-signal sinusoidal perturbation, the impedance response can be approximated by:

$$Z = \frac{V(t)}{i(t)} = \frac{dV}{di} \quad \quad Z_f = \frac{d\eta}{di} = \frac{RT}{\alpha n F} \frac{1}{i} = \left(\frac{RT}{\alpha n F}\right)i_0 e^{\alpha n F \eta_{act}/RT}$$
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**ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)**

**Equivalent circuit models.**

**Electrochemical Reaction:**

\( Z_f \) has no imaginary component and can be represented by a pure resistor \( (Z_f = R_f) \).

A high \( R_f \) indicates a *highly resistive* electrochemical reaction.

The parallel combination of two impedance elements is given by:

\[
\frac{1}{Z_{\text{parallel}}} = \frac{1}{Z_1} + \frac{1}{Z_2}
\]

\[
\frac{1}{Z} = \frac{1}{R_f} + j \omega C_{dl}
\]

\[
Z = \frac{1}{1/R_f + j \omega C_{dl}}
\]
IN SITU ELECTROCHEMICAL CHARACTERIZATION

- ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)

Equivalent circuit models.

Electrochemical Reaction:

The impedance shows a characteristic semicircular response:

\[ \omega = \frac{1}{R_f C_{dl}} \]

Decreasing \( \omega \)
At extremely high frequencies: capacitors act as short circuits. The current can be completely shunted through the capacitor and the impedance of the model is zero.

At extremely low frequencies, capacitors act as open circuit. The current is forced to flow through the resistor and the effective impedance of the model is given by the impedance of the resistor.

At intermediate frequencies: the model will have both resistive and capacitive elements.
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**ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)**

Equivalent circuit models.

Mass transport: can be modelled by Warburg circuit elements.

The impedance of an “infinite Warburg element” (used for an infinitely thick diffusion layer) is given by the equation:

\[ Z = \frac{\sigma_i}{\sqrt{\omega}} (1 - j) \]

\( \sigma_i = \) the Warburg coefficient for a species i.

If the species concentration is low and diffusion is low, \( \sigma_i \) will be large and the impedance due to mass transport can become significant.
IN SITU ELECTROCHEMICAL CHARACTERIZATION

- ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)

Equivalent circuit models.

Mass transport:

At high frequencies the Warburg impedance is small since diffusing reactants do not have to move very far.
Mass transport:

Due to convective mixing in fuel cell flow structures usually restricts the diffusion layer to the thickness of the electrode. In these cases, it is better to use porous bounded Warburg model.

\[ Z = \frac{\sigma_i}{\sqrt{\omega}} (1 - j) \tanh \left( \frac{\delta}{\sqrt{D_i}} \sqrt{j\omega} \right) \]

\( \delta \) = the diffusion layer thickness.

At high frequencies or cases where \( \delta \) is large, the porous bounded Warburg impedance converges to the infinite Warburg behaviour.
IN SITU ELECTROCHEMICAL CHARACTERIZATION

**ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)**

**Equivalent circuit models.**

**Mass transport:**

At low frequencies or for small diffusion layer, the porous bounded Warburg impedance moves back toward the real axis.
**IN SITU ELECTROCHEMICAL CHARACTERIZATION**

**ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)**

Equivalent circuit models.

<table>
<thead>
<tr>
<th>Circuit Element</th>
<th>Impedance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistor</td>
<td>$R$</td>
</tr>
<tr>
<td>Capacitor</td>
<td>$1/j \omega C$</td>
</tr>
<tr>
<td>Constant-phase element</td>
<td>$1/[Q(j \omega)^\alpha]$</td>
</tr>
<tr>
<td>Inductor</td>
<td>$j \omega L$</td>
</tr>
<tr>
<td>Infinite Warburg</td>
<td>$(\sigma_i/\sqrt{\omega})(1-j)$</td>
</tr>
<tr>
<td>Finite (porous bounded) Warburg</td>
<td>$(\sigma_i/\sqrt{\omega})(1-j) \tanh(\delta \sqrt{j \omega/D_i})$</td>
</tr>
<tr>
<td>Series impedance elements</td>
<td>$Z_{series} = Z_1 + Z_2$</td>
</tr>
<tr>
<td>Parallel impedance elements</td>
<td>$1/Z_{parallel} = 1/Z_1 + 1/Z_2$</td>
</tr>
</tbody>
</table>
**IN SITU ELECTROCHEMICAL CHARACTERIZATION**

- **ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)**

**Simple Equivalent Circuit Fuel Cell Model.**

Let's suppose that the fuel cell suffers from the following loss processes:

1. Anode activation
2. Cathode Activation
3. Cathode mass transfer
4. Ohmic loss
IN SITU ELECTROCHEMICAL CHARACTERIZATION

- ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)
### IN SITU ELECTROCHEMICAL CHARACTERIZATION

#### ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)

<table>
<thead>
<tr>
<th>Fuel Cell Process</th>
<th>Circuit Element</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ohmic resistance</td>
<td>$R_\Omega$</td>
<td>10 mΩ</td>
</tr>
<tr>
<td>Anode Faradaic resistance</td>
<td>$R_{fA}$</td>
<td>5 mΩ</td>
</tr>
<tr>
<td>Anode double-layer capacitance</td>
<td>$C_{dlA}$</td>
<td>3 mF</td>
</tr>
<tr>
<td>Cathode Faradaic resistance</td>
<td>$R_{CA}$</td>
<td>100 mΩ</td>
</tr>
<tr>
<td>Cathode double-layer capacitance</td>
<td>$C_{dlA}$</td>
<td>30 mF</td>
</tr>
<tr>
<td>Cathode Warburg coefficient</td>
<td>$\sigma$</td>
<td>0.015</td>
</tr>
</tbody>
</table>
Simple Equivalent Circuit Fuel Cell Model.

In many real fuel cells, the RC loop for the cathode overwhelms the RC loop for the anode.
IN SITU ELECTROCHEMICAL CHARACTERIZATION

- ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)

Simple Equivalent Circuit Fuel Cell Model.

To fully understand fuel cell behaviour, it is essential to measure the impedance response at several different points along a fuel cell’s i-V curve.

The impedance behaviour depends on which loss processes are dominant.

At low currents, the activation kinetics dominate and \( R_f \) is large and the mass transport can be neglected.

A higher currents, \( R_f \) decreases since the activation kinetics improve with increasing \( \eta_{\text{act}} \).

At high currents, mass transport effects occur.
IN SITU ELECTROCHEMICAL CHARACTERIZATION

- ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)

Simple Equivalent Circuit Fuel Cell Model.

Graphs showing cell voltage vs. current and impedance plots.
The current interrupt method can provide some of the same information provided by EIS (but not as accurate and as detailed as EIS)

**Advantages**

- Extremely fast;
- Simpler measurements hardware;
- Implemented on high-power fuel cell systems;
- Conducted in parallel with j-V curve measurement.
IN SITU ELECTROCHEMICAL CHARACTERIZATION

- CURRENT INTERRUPT MEASUREMENT

(a) Diagram showing electrical components: $R_\Omega$, $C_{dl}$, $R_f$, and $Z_W$.

(b) Graph showing current (A) as a function of time (t), with current at 0.5 A.

(c) Graph showing voltage (V) as a function of time (t), with voltage at 1.0 V.
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CURRENT INTERRUPT MEASUREMENT

Basic idea

When a constant-current load on a fuel cell system is abruptly interrupted, the resulting time-dependent voltage response will be representative of the capacitive and resistive behaviour of the various components in the fuel cell.

Interruption of the current induces:

- An immediate rebound in the voltage: ohmic resistance of the fuel cell

- An additional, time-dependent rebound in the voltage: associated with the much slower reaction and mass transport processes.

Voltage-time response can be used to separate the two contributions.
IN SITU ELECTROCHEMICAL CHARACTERIZATION

- CURRENT INTERRUPT MEASUREMENT

![Diagram of an electrical circuit with components labeled $R_\Omega$, $C_{dl}$, $R_f$, and $Z_w$.](image)

![Graph showing current (A) over time (t).](image)

![Graph showing voltage (V) over time (t).](image)
CURRENT INTERRUPT MEASUREMENT

Useful method for determining the ohmic component of fuel cell loss at each measurement point on the fuel cell i-V curve.

After a fuel cell i-V data point is recorded, a current interrupt measurement is then made to determine $R_Ω$ at that point.

The ohmic-loss portion of the i-V curve data can then be removed; such curves are called « iR-free » or « iR-corrected » i-V curves.

The result is a nearly complete quantification of the ohmic, activation and concentration losses associated with the fuel cell.
EX SITU ELECTROCHEMICAL CHARACTERIZATION

- Porosity determination;
- BET surface Area determination
- Gas permeability
- Structure determinations: Optical microscopy (OM), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM) and X-Ray diffraction measurements.
- Chemical determinations