



UNIVERSITÀ
DEGLI STUDI
DI TRIESTE



Dipartimento di
Ingegneria
e Architettura

ELECTROCHEMICAL MEASUREMENTS (FOR FUEL CELLS AND BATTERIES)

Prof. Marco Bogar

A.A. 2023-2024

INTRODUCTION

Electrochemical Characterization Techniques (*In Situ*)

These techniques use the electrochemical variables of voltage, current, and time to characterize the performance under operating conditions of either a single component or the full assembly of an electrochemical device.

***Ex Situ / In Situ* Complementary Characterization Techniques**

These techniques characterize the detailed structure or properties of the individual components composing the fuel cell, but generally only components removed from the device in an unassembled, non-functional form.

Advanced Characterization Techniques (*Ex Situ / In Situ*)

These techniques characterize the detailed structure or properties of the individual components inside the device.

OVERVIEW OF CHARACTERIZATION TECHNIQUES

Electrochemical Characterization Techniques (*In Situ*)

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Ex Situ / In Situ Complementary Characterization Techniques

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IN SITU ELECTROCHEMICAL CHARACTERIZATION

In any electrochemical experiment, the three fundamental variables to be monitored are voltage, current, and time.

Moreover, the following distinction can be highlighted:

- **Voltage-controlled.** The voltage of a system is controlled by the user and the resulting current response is measured. Voltage can be either kept in steady state (*potentiostatic*, where the control voltage is constant in time) or dynamic (where the control voltage varies with time).
- **Current-controlled.** The current of a system is controlled by the user and the resulting voltage response is measured. Current can be either kept in steady state (*galvanostatic*, where the control current is constant in time) or dynamic (where the control current varies with time).

Measurements carried out in different dynamical ranges may lead to different outputs due to the fact that electrochemical kinetics could evolve differently depending on the frequency of the probe used.

OUTLOOK / *IN SITU* ELECTROCHEMICAL CHARACTERIZATION



Polarization curve

Cyclic Voltammetry

Linear Sweep Voltammetry

Tafel plots

Electrochemical Impedance Spectroscopy

Total Harmonic Distortion

OUTLOOK / *IN SITU* ELECTROCHEMICAL CHARACTERIZATION

Polarization curve

Cyclic Voltammetry

Linear Sweep Voltammetry

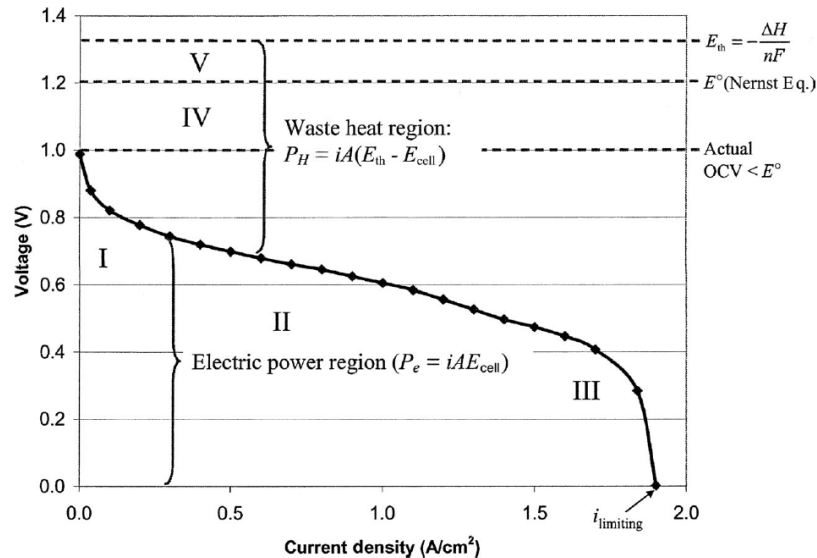
Tafel plots

Electrochemical Impedance Spectroscopy

Total Harmonic Distortion

CURRENT - VOLTAGE MEASUREMENTS / FUEL CELLS

1. Quantification of device losses



I. Activation (kinetic) overpotential at the electrodes.

II. Ohmic polarization of the fuel cell. This includes all electrical and ionic conduction losses through the electrolyte, catalyst layers, cell interconnects, and contacts.

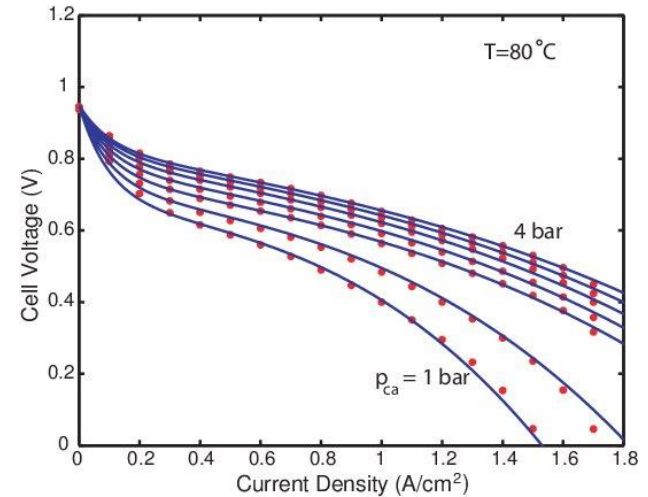
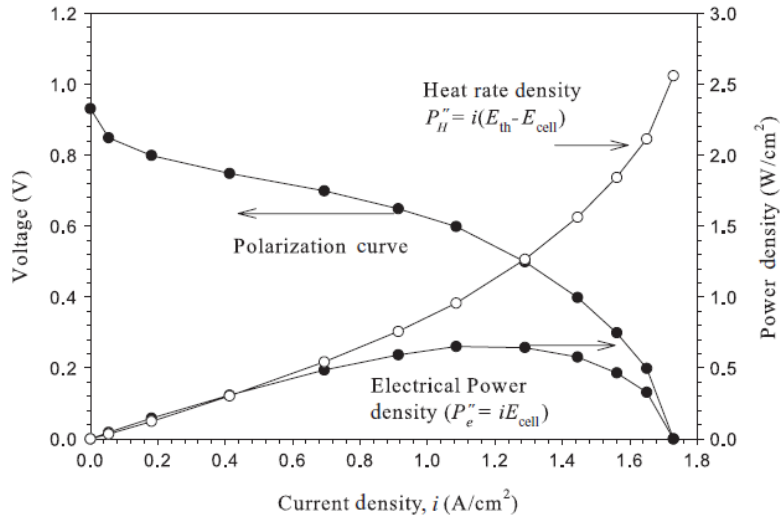
III. Concentration polarization of the fuel cell, caused by mass transport limitations of the reactants to the electrodes.

IV. Departure from the Nernst thermodynamic equilibrium potential. This loss can be very significant and can be due to undesired species crossover through the electrolyte, internal currents from electron leakage through the electrolyte, or other contamination or impurity.

V. Departure from the maximum thermal voltage, a result of entropy change which cannot be engineered.

CURRENT - VOLTAGE MEASUREMENTS / FUEL CELLS

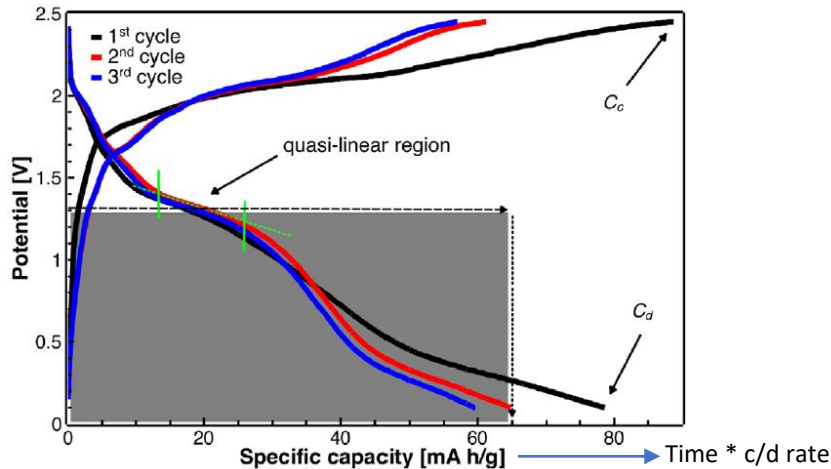
2. Comparison of fuel cell performances by means of polarization curve, waste heat generation and useful electrical power generation rate density.



2002, Proc. ASME 2002 Int. Mech. Eng. Congress,
Pukrushpan <https://doi.org/10.1115/IMECE2002-32051>

CURRENT - VOLTAGE MEASUREMENTS / BATTERIES

1. Comparison of batteries performances: direct calculation of coulombic efficiency



Exploring an Aluminum Ion Battery Based on Molybdate as Working Electrode and Ionic Liquid as Electrolyte
R. Borah et al. / Materials Today Advances 6 (2020) 100046

$$\eta = \frac{C_d \text{ at the end of the discharging time}}{C_c \text{ at the end of the charging time}}$$

In the example:

$$\eta_{2^{nd} \text{ cycle}} = 94.4\%$$

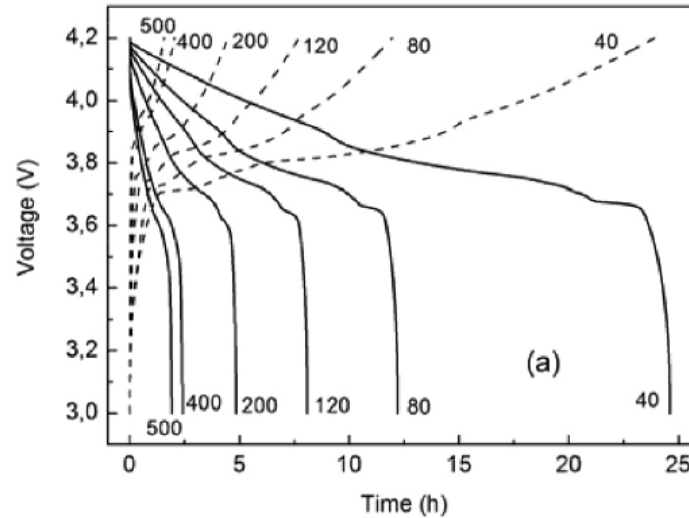
$$\eta_{3^{rd} \text{ cycle}} = 95.6\%$$

This is a very typical example, where some energy is required in the first cycle to equilibrate the battery chemistry. Then, η approaches 100% in the following cycles.

Capacity measurements are used to define battery lifetime (end: when charged charge is below the 80% of initial value, recorded after the first 5 cycles for equilibration requirements)

CURRENT - VOLTAGE MEASUREMENTS / BATTERIES

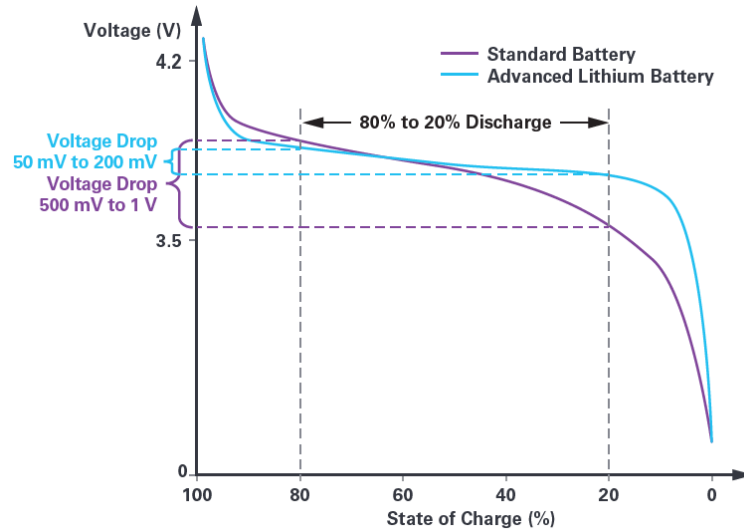
2. Discharge curves as a tool for battery characterization



Quim. Nova, Vol. 39, No. 8, 901-905, 2016

CURRENT - VOLTAGE MEASUREMENTS / BATTERIES

3. Charge/Discharge cycling curves as a comparative tool and a guideline for system design



Higher Reliability, Safety, and 30% Longer Lifetime with Advanced Battery Management in Healthcare Energy Storage Systems, Stefano Gallinaro, Analog Devices

Battery performances vary according to the application (in example electric vehicle is different that stationary power supply). In any case, a very flat discharge curve at a nominal voltage range is always desired.

In example, the flatter the curve, the higher the efficiency of the system in which batteries are installed.

As a drawback, SOC and SOH are harder to be identified and a more sophisticated protocol for avoiding overcharge has to be taken into account

CURRENT - VOLTAGE MEASUREMENTS / BATTERIES

4. Chronopotentiometry (galvanostatic voltammetry) involves the study of voltage transients at an electrode upon which is imposed a constant current. Used for investigating process kinetics at the electrodes

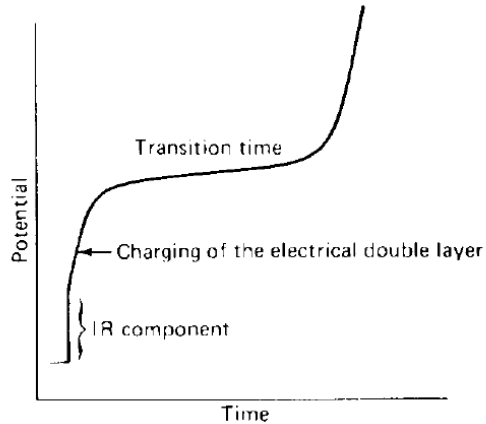
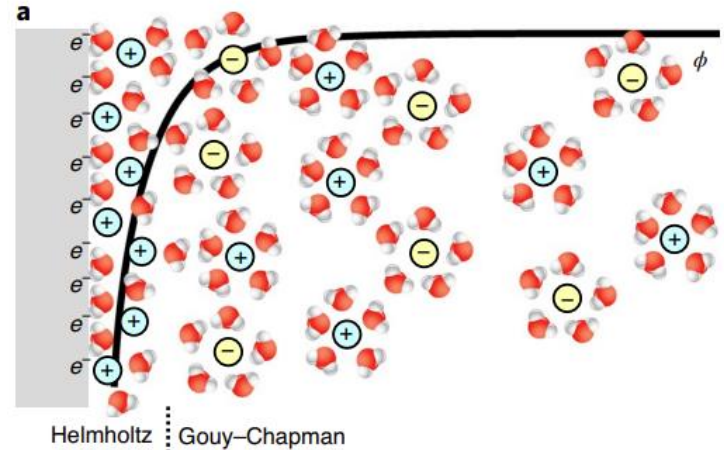


FIGURE 2.28 Chronopotentiogram of a system with significant resistance.



Swift et al., *Nature Computational Science* 1, pages212–220 (2021)

OUTLOOK / *IN SITU* ELECTROCHEMICAL CHARACTERIZATION

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Linear Sweep Voltammetry

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CYCLIC VOLTAMMETRY

Cyclic voltammetry (CV) is one of the most widely used electrochemical techniques and it is frequently applied for the initial characterization of a redox system. It allows to:

- Define the number of oxidation state of the specimen under investigation.
- Retrieve qualitative information about the oxidation state stability and the electron transfer kinetics.
- Retrieve quantitative information of redox potentials of the electroactive species
- Evaluate of the effect of different materials, morphology, or operating environments upon the redox process.

Moreover:

- It is non-destructive and does not require the device to be disassembled during operation
- It can be used on single electrodes (half-cell) or on the entire device.

THE POTENTIOSTAT



https://www.metrohm.com/it_it/prodotti/elettrochimica/modular-line.html

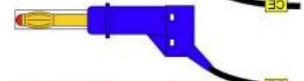


<https://www.biologic.net/topics/what-is-a-potentiostat-how-potentiostats-work-and-their-use-in-science-and-industry/>

Counter electrode (CE)



Reference electrode (RE)



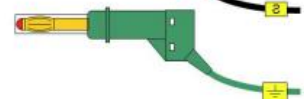
Working electrode (WE)



Sense (S)

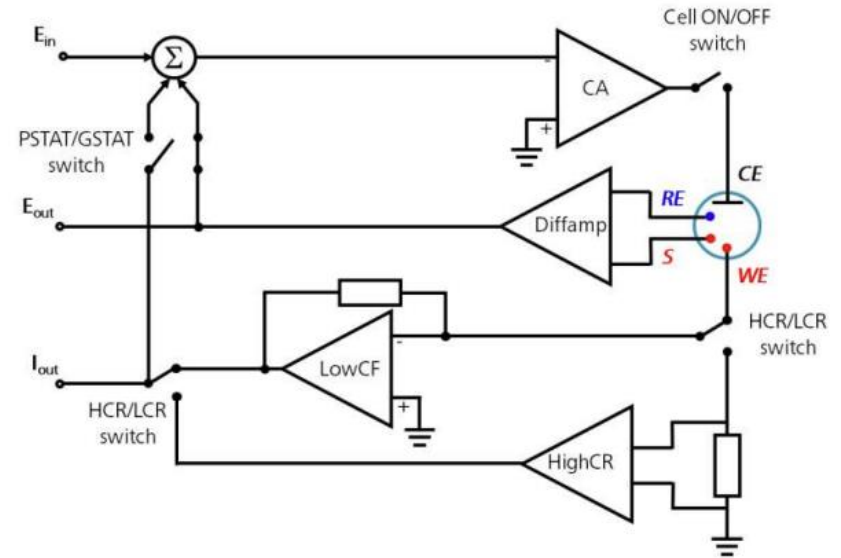
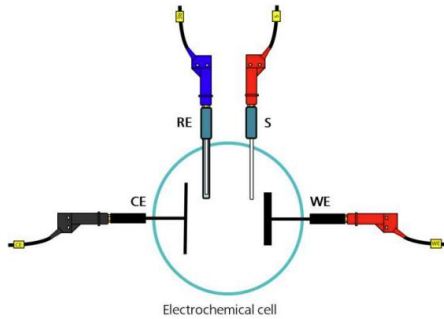
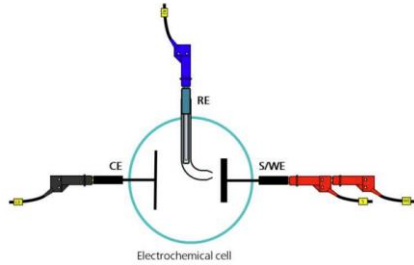
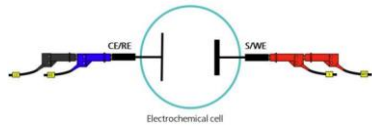


Ground connection (\oplus)



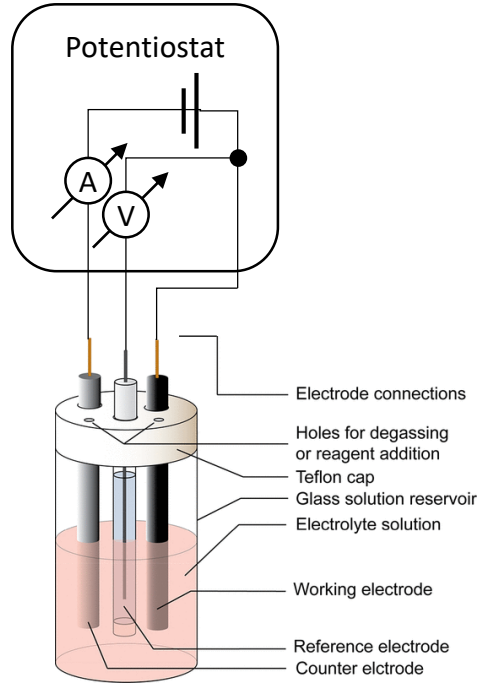
Basic overview of the working principle of a potentiostat/galvanostat (PGSTAT) – Electrochemical cell setup
www.metrohm.com/en/products/electrochemistry

THE POTENTIOSTAT

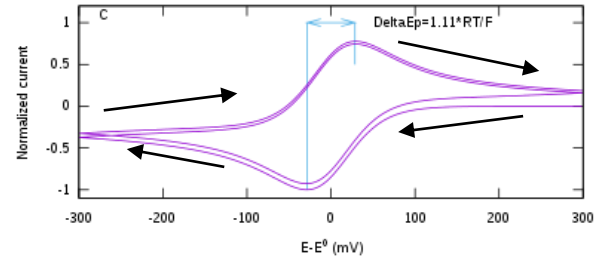
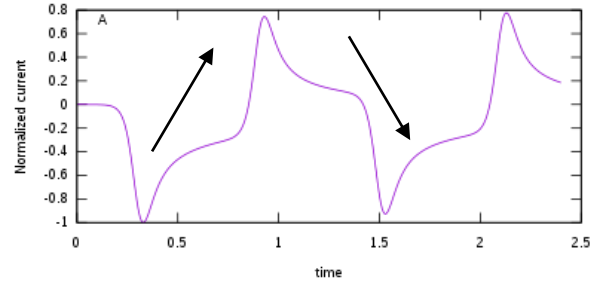
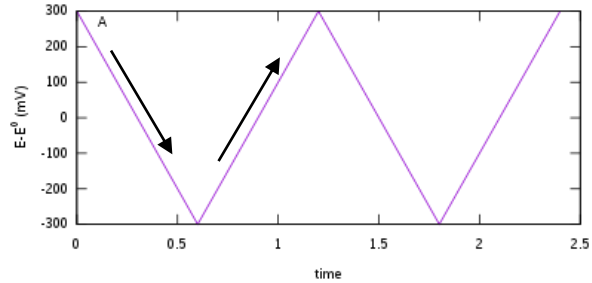


Basic overview of the working principle of a potentiostat/galvanostat (PGSTAT) – Electrochemical cell setup
www.metrohm.com/en/products/electrochemistry

CYCLIC VOLTAMMETRY



Elgrishi N., *J. Chem. Educ.* 2018, 95, 2, 197–206



Main parameters to set

- Upper and lower potentials
- Scan rate (V/s)

Main features to be interpreted

- Peaks
- Plateau regions

CYCLIC VOLTAMMETRY

In alkaline media

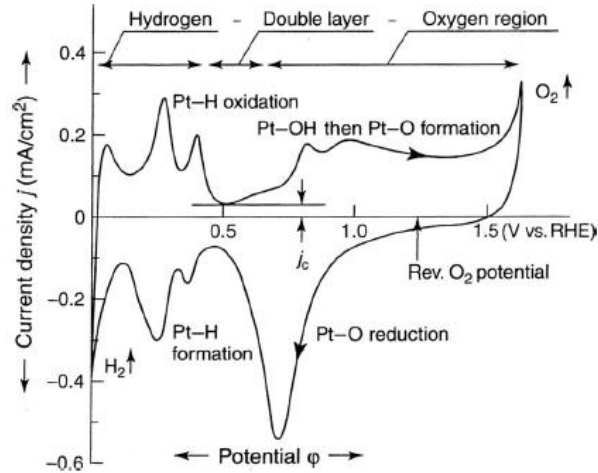


Figure 9.8 Cyclic voltammogram of polycrystalline platinum in 1 M KOH alkaline electrolyte solution at 20°C with voltage sweep rate of 100 mV/s. (Reproduced with permission from Ref. [12].)

HOR	$Pt - H + OH^- \rightarrow Pt + H_2O + e^-$
Pt oxidation	$Pt + OH^- \rightarrow Pt - OH + e^-$ $Pt - OH + OH^- \rightarrow Pt - O + H_2O + e^-$
OER	$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$
ORR	$Pt + H_2O + e^- \rightarrow Pt - H + OH^-$
HER	$2H_2O + 2e^- \rightarrow 2OH^- + H_2$

CYCLIC VOLTAMMETRY

In acidic media

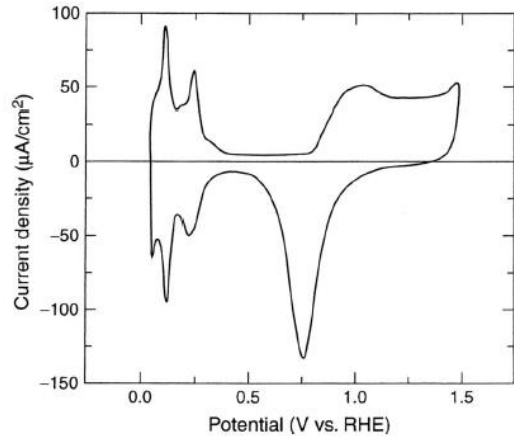


Figure 9.9 CV of polycrystalline platinum in acid 0.5 M H_2SO_4 electrolyte solution with voltage sweep rate of 50 mV/s. (Reproduced with permission from Ref. [12].)

HOR	$Pt - H + H_2O \rightarrow Pt + H_3O^+ + e^-$
Pt oxidation	$Pt + H_2O \rightarrow Pt - OH + e^- + H^+$ $Pt - OH + H_2O \rightarrow Pt - O + H_3O^+ + e^-$
OER	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$
ORR	$Pt + H_3O^+ + e^- \rightarrow Pt - H + H_2O$
HER	$2H_3O^+ + e^- \rightarrow 2H_2O + H_2$

CYCLIC VOLTAMMETRY / ECSA

By means of CV it is possible to quantify the electrochemically active surface area (ECSA), which is one of the most important parameters used to quantify the catalyst active surface, to compare different electrode formulations and/or compositions, and it can be used for describing the degradation of the electrode over time. It is calculated basing on two assumptions:

1. Each platinum site can adsorb only one hydrogen proton.
2. Every available platinum site will be occupied with hydrogen during the transition from hydrogen adsorption to hydrogen evolution.

CYCLIC VOLTAMMETRY / ECSA

It is calculated as:

$$ECSA(\text{cm}^2/\text{g}) = \frac{Q_{H,ad}(\text{C}/\text{cm}^2)}{m(\text{g}/\text{cm}^2) * C(\text{C}/\text{cm}^2)}$$

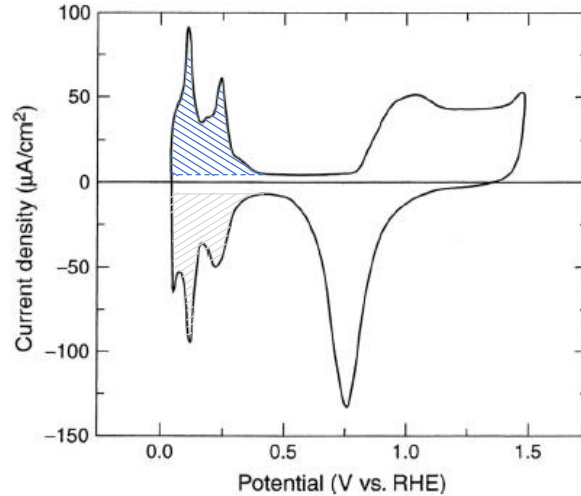
$Q_{H,ad}$ - hydrogen adsorption charge (C/cm^2)

m – Pt mass loading (g/cm^2)

C – is a proportionality constant

relating charge and catalyst area;

for polycrystalline Pt: $C = 210 \mu\text{C}/\text{cm}^2$

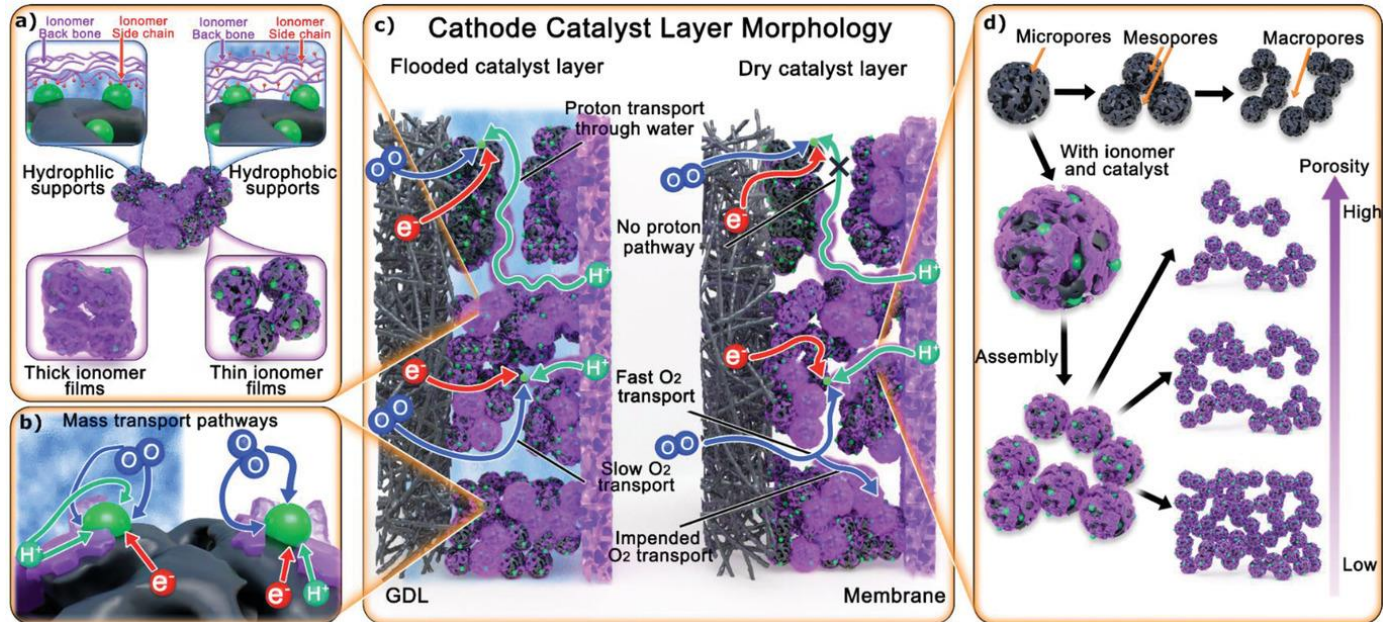


For calculating the hydrogen adsorption charge the area underneath the hydrogen adsorption peaks is integrated:

$$Q_{H,ad} = \int I(t)dt$$

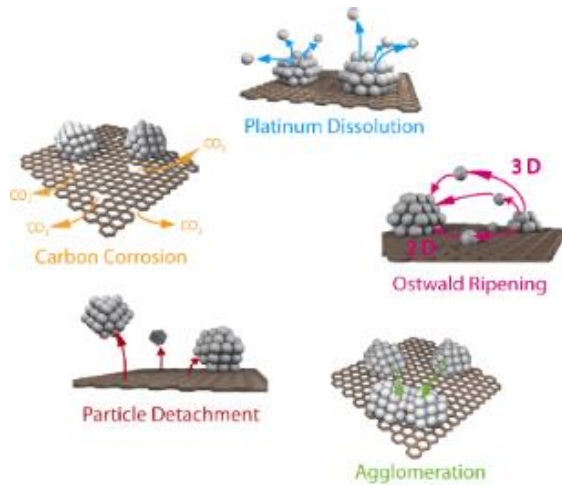
And the baseline for integration is set from the low-potential-end-side of the formation of the double layer

ECSA REDUCTION

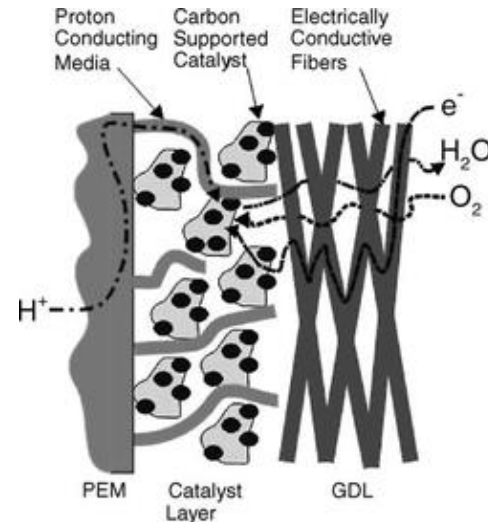


Theo, Adv. Energy Mater. 2021, 11, 2101025, DOI: 10.1002/aenm.202101025

ECSA REDUCTION



Meier, Nanotechnol. 2014, 5, 44–67. doi:10.3762/bjnano.5.5



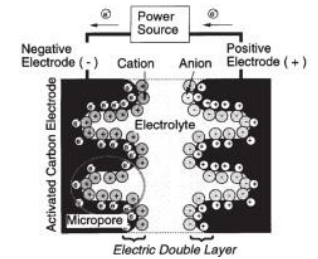
https://en.wikipedia.org/wiki/Membrane_electrode_assembly

CYCLIC VOLTAMMETRY / DOUBLE LAYER CAPACITANCE

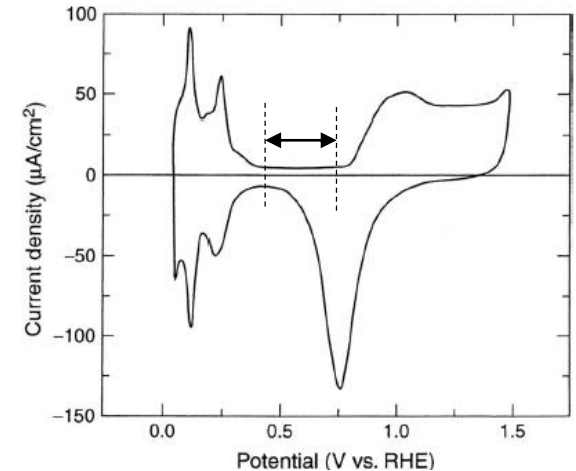
When an electrode surface is subjected to a voltage ramp, a steady-state capacitive current is observed in a short time (i_c) if the only process taking place within the voltage range is the charging of the double layer, that is, movement of ions on either side of an electrode/electrolyte interface. For ideal capacitors, i_c is related to the capacitance (C_{DL}) and to the scan rate (ν):

$$i_c = \nu C_{DL}$$

A possible approach for determining the double layer capacitance consist in recording CVs at various scan rates within a potential region where no redox processes take place, extracting i_c from the anodic and cathodic scans of the recorded voltammograms, and subsequently extracting C_{DL} from the slope of the resulting i_c vs ν plot



<https://doi.org/10.1016/B978-008044163-4/50027-9>



CYCLIC VOLTAMMETRY / ON FUEL CELLS

- N_2 is used instead of O_2 for delating the background noise due to spurious hydrogen adsorption in addition to the hydrogen evolution/oxidation reaction.
- The potential reference is set at the hydrogen oxidation potential by connecting both RE and CE to the anode

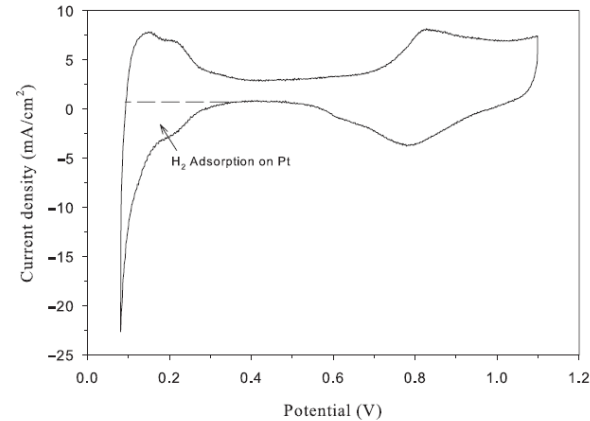
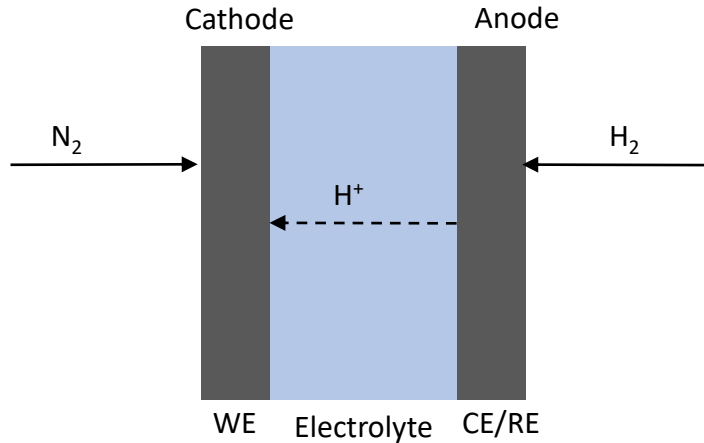


Figure 9.10 The area shown under the dashed line represents hydrogen adsorption and can be used to determine electrochemically active catalyst area. CV done on a 5 cm² active area fuel cell, in-situ. 50 sccm hydrogen on anode, 200 sccm nitrogen on cathode. RH anode/cathode = 100/100%, scan rate 20 mV/sec.

CYCLIC VOLTAMMETRY / ON FUEL CELLS

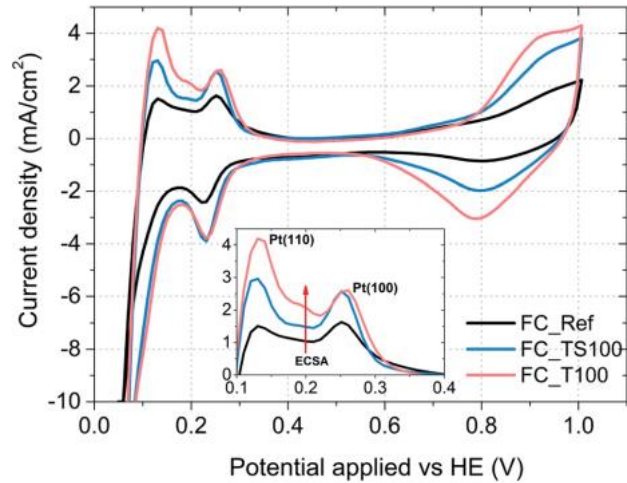


Fig. 9 Cyclic voltammograms of fuel cells and characteristic desorption peaks assigned to the Pt(110) and Pt(100) crystal surface of the catalyst (inset); potential applied versus fuel cell anode.

Malinowski, RSC Adv., 2019,9, 24428-24439

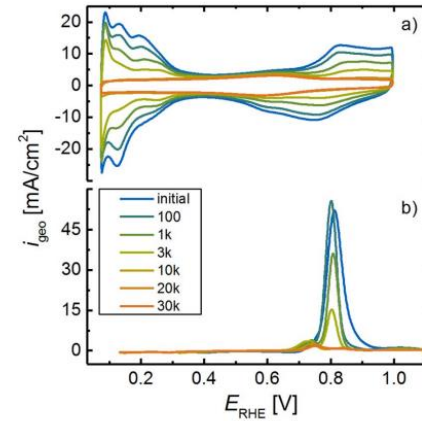
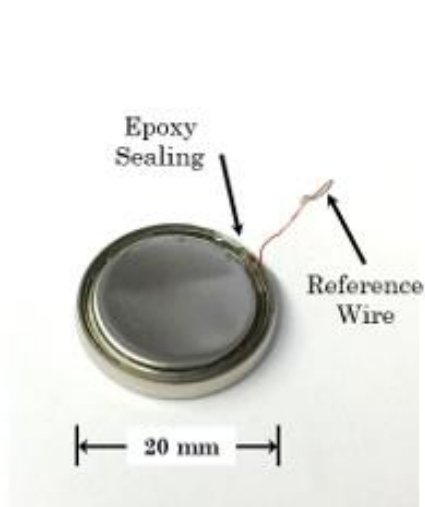


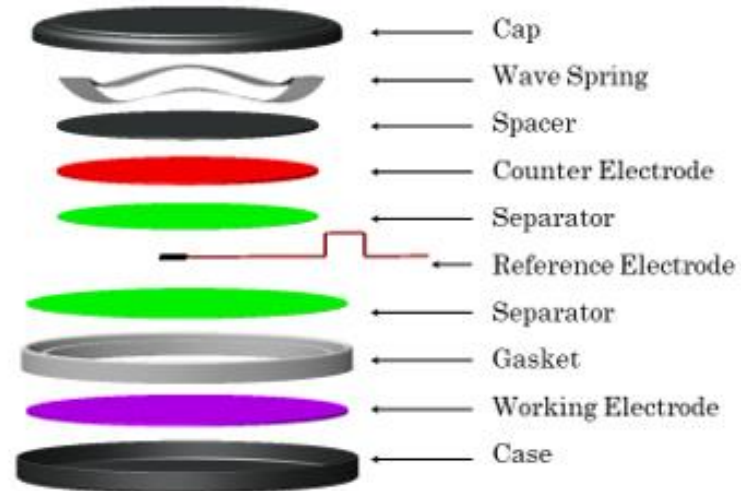
Figure 4. a) CVs of the cathode after different aging stages during a SW-based AST between 0.6 and 1.0 V_{RHE} (see Figure 2b). CVs were conducted at a scan rate of 150 mV/s from 0.07 to 1.00 V_{RHE} at ambient pressure and 40°C (the anode was supplied with 200 ncm of 5% H₂ (in N₂) and the cathode N₂ flow was 50 ncm (set to zero flow when recording the CVs)). b) CO stripping voltammograms after subtraction of the subsequent anodic sweep, recorded at a scan rate of 100 mV/s to 1.1 V_{RHE} at 150 kPa_{abs} and 40°C (constant flows of 200 ncm 5% H₂ on the anode and 5 ncm N₂ on the cathode). CO was adsorbed for 10 min at a flow rate of 100 ncm prior to the CV, maintaining the potential at 0.1 V_{RHE}. To remove residual CO gas from the cell and the test station, a purging procedure with N₂, lasting approximately 1.5 h was executed.

Harzer, 2018 J. Electrochem. Soc. 165 F3118

CYCLIC VOLTAMMETRY / ON BATTERIES



(a)



(b)

Minter et al., *J. Vis. Exp.* (135), e57735

CYCLIC VOLTAMMETRY / ON BATTERIES

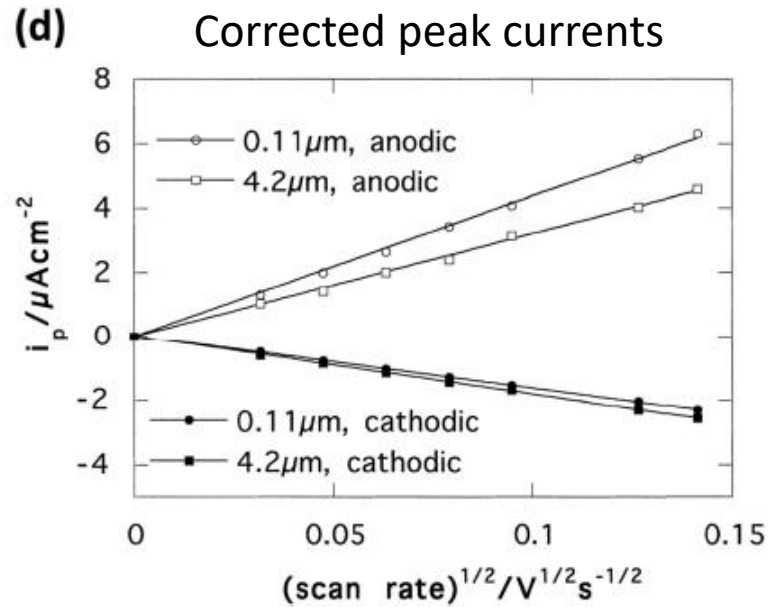
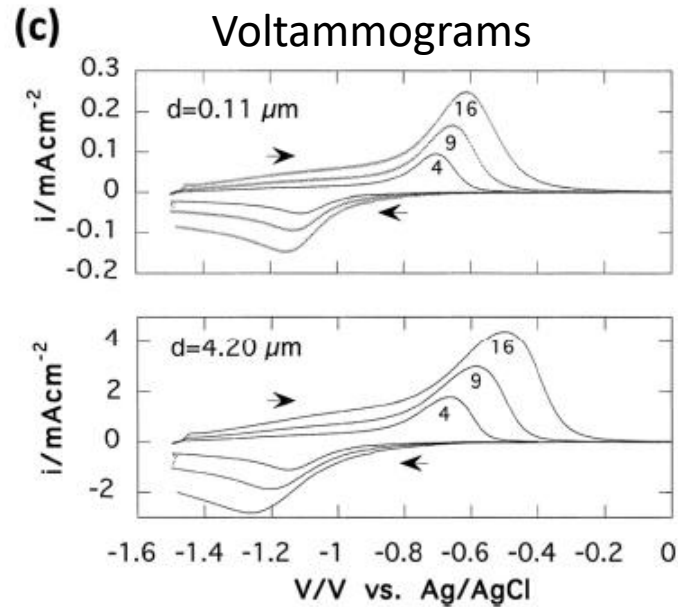
Diffusion coefficient can be estimated by comparing results obtained at different scan rates from the Randles–Ševčík equation:

$$i_p = 0.4463nFAC \sqrt{\frac{nFvD}{RT}}$$

The comparison of CV allows thus also to perform size-dependant analysis. The effects on size change are observable as a shift in redox peaks.

CYCLIC VOLTAMMETRY / ON BATTERIES

CV analysis on two TiO_2 electrodes having different sizes: 0.11 and 4.20 μm



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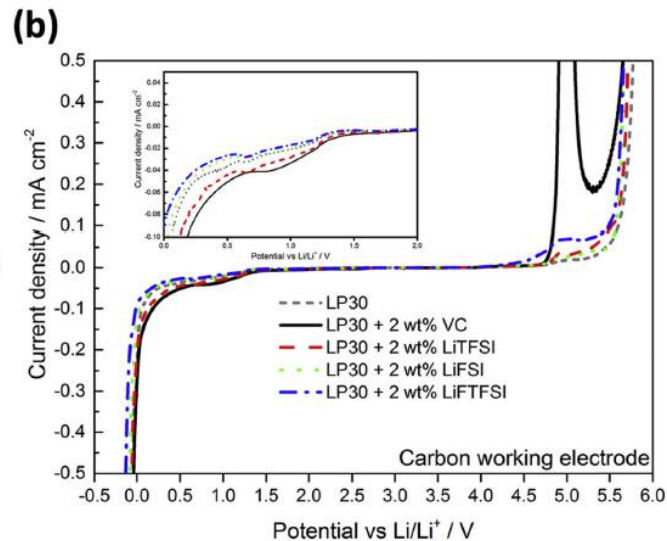
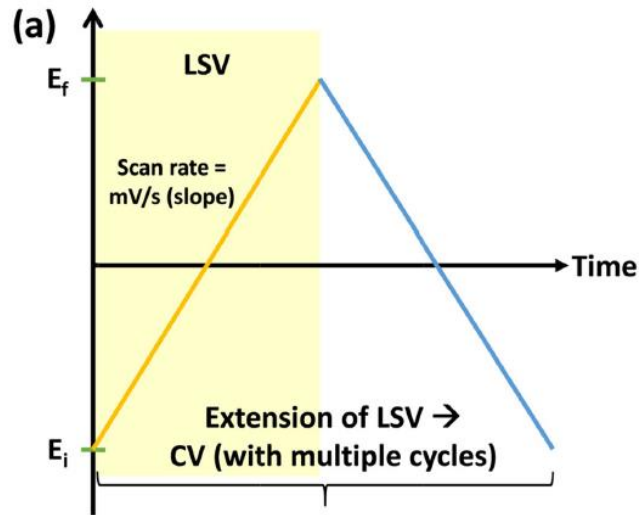
Electrochemical Impedance Spectroscopy

Total Harmonic Distortion

LINEAR SWEEP VOLTAMMETRY/ BATTERIES

LSV was here used for determining the electrochemical stability of an electrolyte with or without stabilizers for a graphite||LiFePO₄ battery.

- shift of the reduction peak



OUTLOOK / *IN SITU* ELECTROCHEMICAL CHARACTERIZATION

Polarization curve

Cyclic Voltammetry

Linear Sweep Voltammetry

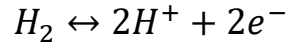
Tafel plots

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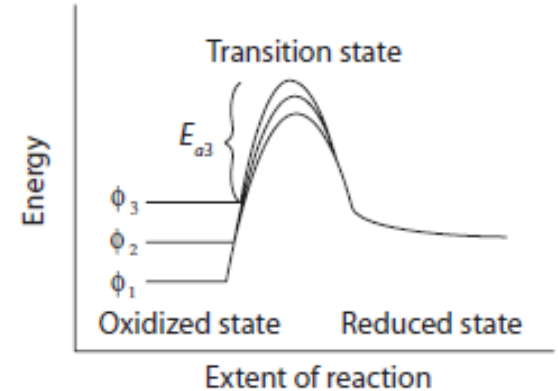
TAFEL PLOTS

Let's consider an individual electrode, initially at equilibrium. For example, the global HOR:



At equilibrium (open circuit), this reaction actually proceeds in both directions across the anode double layer, with no *net* reaction in either direction. Some hydrogen is being oxidized, and an equivalent amount is being reduced (electrons involved in these redox processes constitute the exchange current density j_0)

To maintain a net reaction rate in a given direction, a small activation overpotential η is required to be set.



TAFEL PLOTS / THE BUTLER-VOLMER EQUATION

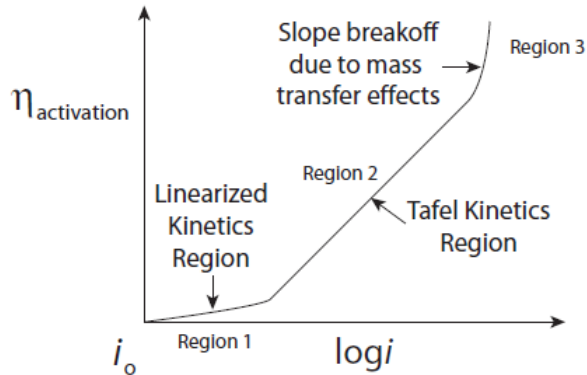
The balance among the overpotentials and the net current density at the electrode is defined by the BV equation:

$$j_{cell} = j_0 \left(e^{I \eta \alpha_a F / RT} - e^{-II \eta \alpha_c F / RT} \right)$$

I and *II* represent, respectively, the oxidation and the reduction reaction at the particular electrode, j_{cell} is the cell total current density, j_0 is the exchange current density of the electrode of interest, η is the activation overpotential at the given electrode, α_a is the anodic charge transfer coefficient, the fraction of the activation polarization energy of reaction that goes toward enhancing the oxidation branch of the reaction at a given electrode, α_c is the fraction of the additional activation polarization energy of the reaction that goes into enhancing the reduction branch of the equilibrium; $\alpha_a + \alpha_c = n$, where n is the number of electrons transferred in the *elementary* reaction step for the electron transfer. Experimentally, this value is often found to be a non integer between 1 and 2 due to multiple charge transfer reactions. The fundamental assumption of the BV kinetic model is that the reaction is rate limited by a single electron transfer step, which may not actually be true.

TAFEL PLOTS

Additional polarization required or increasing current is greatly increased after the low-currents threshold value. Defining the exchange current density j_0 is of preeminent importance, as it is a measure of the effectiveness of the electrode in promoting the electrochemical reaction and is the electrode reaction exchange at equilibrium.



BV equation can be linearized when the electrode polarization can be considered to be very low ($x < 0.15$): in this region $e^x \cong 1 + x$ (Taylor expansion), and:

$$j_{\text{cell}} \cong j_0 \left[\left(1 + \eta \frac{\alpha_a F}{RT} \right) - \left(1 + \eta \frac{-\alpha_c F}{RT} \right) \right]$$

Which leads to:

$$\eta = \frac{j}{j_0} \frac{RT}{(\alpha_a + \alpha_c)nF} = \frac{j}{j_0} \frac{RT}{nF}$$

TAFEL PLOTS

In the middle region, the Tafel approximation (stating that one of the two current branches dominating) can be used:

$$j_{cell} = j_0 [\pm e^{\eta(\pm\alpha_k F/RT)}] \Rightarrow \eta = \pm \frac{RT}{\alpha_k F} \ln\left(\frac{j}{j_0}\right)$$

From where: $\eta = a + b \log j$

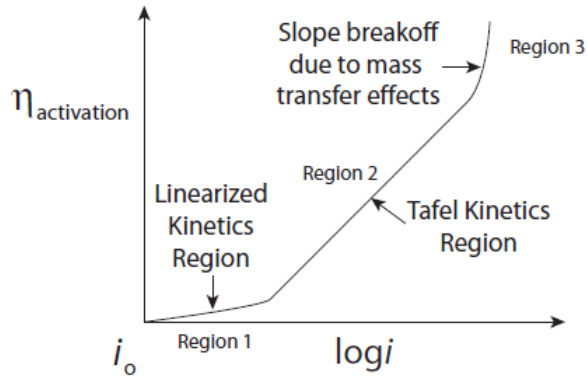
With the constant a defined as:

$$a = 2.303 \frac{RT}{\alpha_k F} \log j_0$$

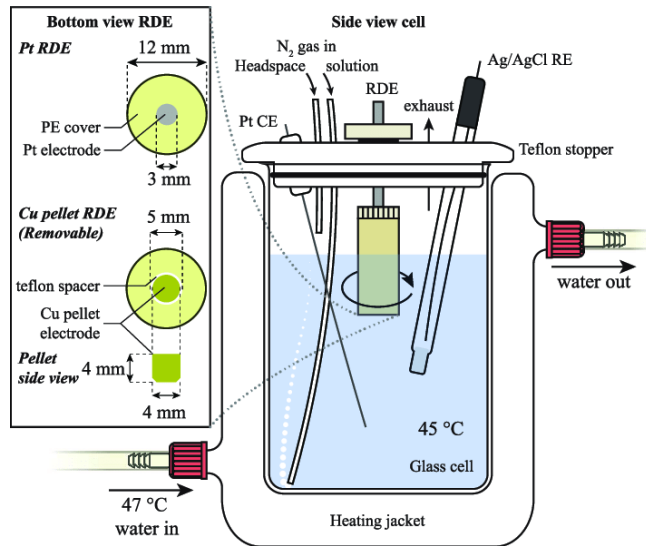
And the Tafel slope, b , defined as:

$$b = -2.303 \frac{RT}{\alpha_k F}$$

With k describing the dominant branch of the reaction



TAFEL PLOTS / ON FUEL CELLS



Karel P. S. Haesevoets *et al* 2019 *J. Electrochem. Soc.* **166** D315

Electrode kinetics are usually tested and optimized at first by means of laboratory instrumentation with the Rotating Disk Electrode setup, where The rotation rate is used to eliminate concentration polarization, and ohmic, nonuniformity, and crossover effects are all eliminated or corrected for, so that only the pure kinetic response of the electrode of interest is examined.

TAFEL PLOTS / ON FUEL CELLS

Tafel plots can be also retrieved from fuel cell devices: the anode is used as a dynamic hydrogen electrode, thus constituting a pseudo reference electrode, while the cathode becomes the electrode of interest, and all losses are assumed to come from ohmic, crossover (if applicable), and oxidizer reduction reaction (ORR):

$$E_{cell} = E^0(T, P) - |\eta_{a,c}| - \eta_r - \eta_x$$

the cell *corrected* voltage versus *effective* current density is plotted on a logarithmic scale

TAFEL PLOTS / REACTION KINETICS

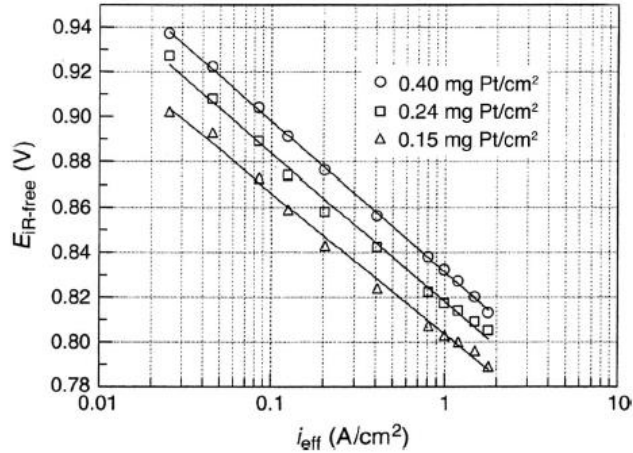


Figure 9.11 Tafel slope preparation from corrected polarization curve data. Data are taken for a 50-cm² fully humidified PEFC at 80°C, 270-kPa anode and cathode in a hydrogen/oxygen environment, for different mass loadings of platinum catalyst. Data are corrected for measured ohmic losses and crossover. (Reproduced with permission from Ref. [15].)

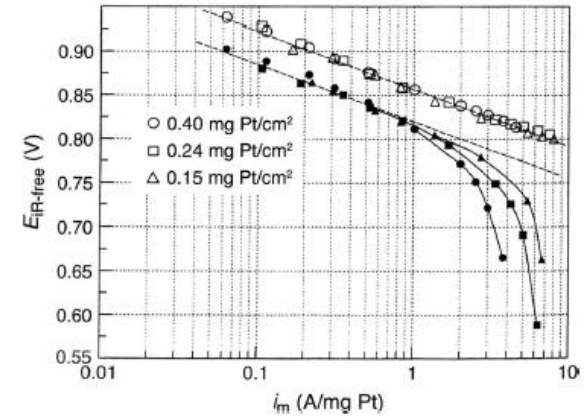


Figure 9.12 Tafel slopes for PEFC electrodes in 50-cm² hydrogen/air environment and hydrogen/oxygen PEFC for different mass loadings of platinum catalyst on mass specific current–density basis (A/mg Pt). Data are taken from fuel cell polarization curves of a fully humidified PEFC at 80°C, 270-kPa anode and cathode. Data are corrected for measured ohmic losses and crossover, but not concentration losses, which results in deviation from Tafel slope at high current density. (Reproduced with permission from Ref. [15].)

From the Tafel slope, the charge transfer coefficient can be determined, and from the intercept the exchange current density can be found

OUTLOOK / *IN SITU* ELECTROCHEMICAL CHARACTERIZATION

Polarization curve

Cyclic Voltammetry

Linear Sweep Voltammetry

Tafel plots

Electrochemical Impedance Spectroscopy

Total Harmonic Distortion

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

EIS is a technique which is widely used in different fields dealing with electrochemistry due to its versatility and the depth of information which can provide.

For a redox system, ohmic contributions, such as ionic and electronic ohmic resistance in the electrolyte and through the other components, can be studied using direct current techniques.

Though, the nonohmic contributions, such as adsorption processes at the electrodes, the charge transfer across the double layer, and the kinetically based concentration polarization, normally have frequency-dependent response times which make them ideal for study using alternating current techniques.

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

EIS is thus carried out by applying a small AC perturbation to a (running) system. Frequency-dependant phenomena will start oscillate at the same frequency of the applied stimulus. An EIS measurement is thus conducted by analysing the behaviour of the system (or from a part of it only) within a defined range of frequencies.

The measured AC current is thus phase shifted according to the whole impedance value of the electrode/fuel cell. In order to correctly carry out the measure, AC signal must be small, that is, perturbation should be that small to be considered linear.

$$\omega = 2\pi f$$

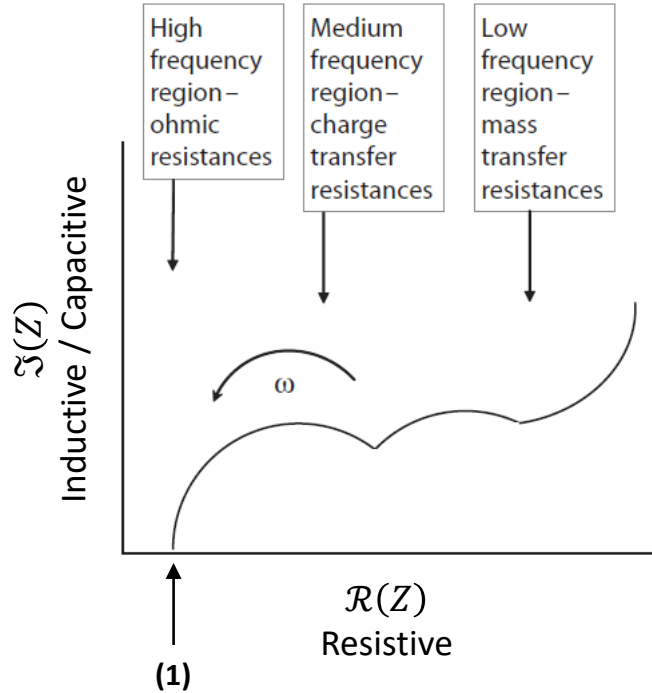
$$Z = \frac{E(t)}{I(t)} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \theta)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \theta)}$$

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

Requirements:

- **Linearity** In general, electrochemical systems are non-linear (*e.g.* the current produced it follows the Butler–Volmer equation). Usually, when perturbations of a system from equilibrium are small, system response can be approximated with a linear model. Therefore, the amplitude of applied AC signal must be small enough to ensure a linear relation between perturbation and response during the entire measurement.
- **Causality** The response measured from the system must be directly originated from the applied AC perturbation.
- **Stability** The system must be returned to its original state without significant alteration after the applied AC perturbation is eliminated.
- **Finiteness** The measured impedance must be a finite value at the whole range of measurement frequency

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY / THE NYQUIST PLOT

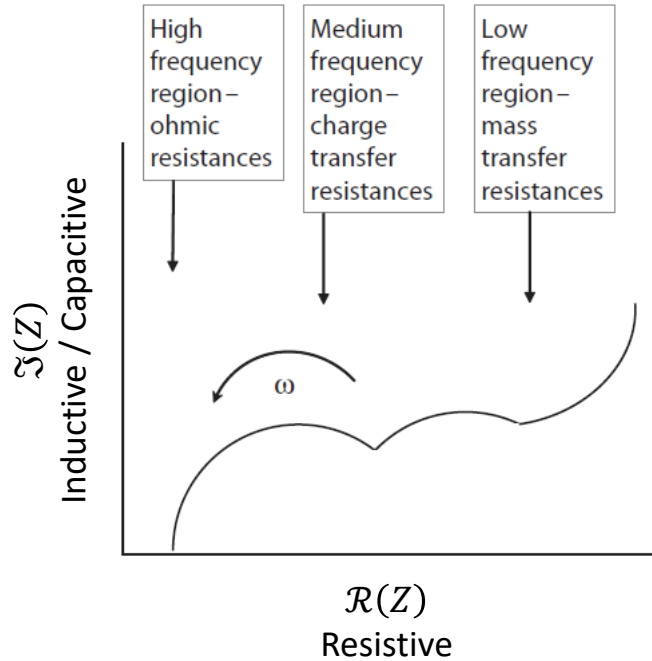


High frequency region:

$$Z_c = X_c = \frac{1}{2\pi f C} \Rightarrow X_c \Big|_{f \rightarrow \infty} \rightarrow 0$$

In (1) the High Frequency Resistance value is found: it is the sum of all of the ohmic resistances of the system (such as, for fuel cells: contact losses, ionic losses in the electrolyte and electronic resistance).

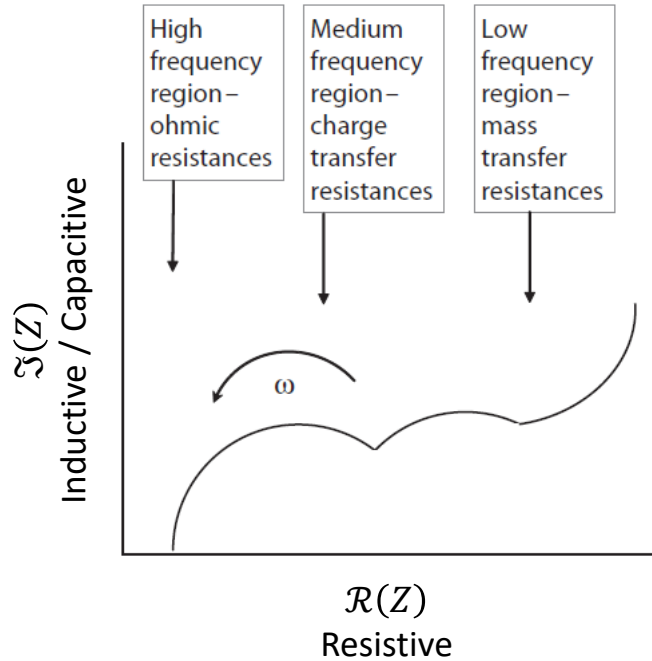
ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY / THE NYQUIST PLOT



Medium frequency region:

The presence of a (positive) semicircle indicates a capacitive process is taking place (such as: charge transfer across the double layer). The semicircle can be represented by a RC-parallel electric circuit, composed by the charge-transfer resistance and the charge-transfer capacity. The circle diameter is equal to the charge transfer resistance.

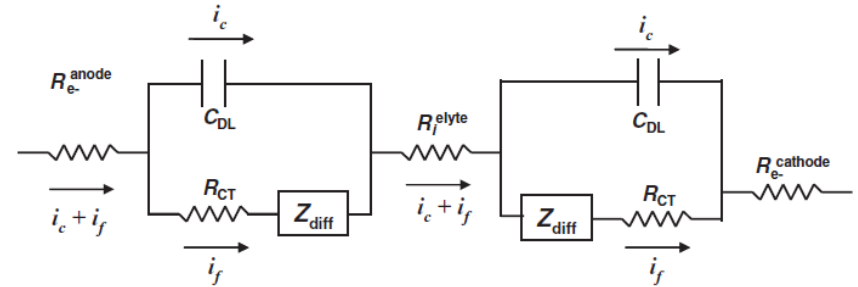
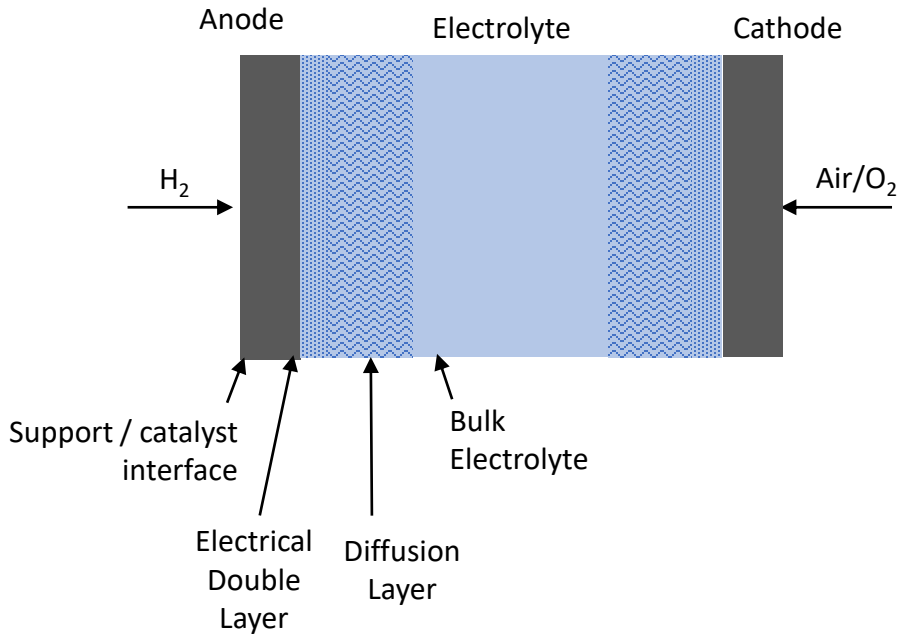
ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY / THE NYQUIST PLOT



Low frequency region:

Mass transport phenomena are related to the evolution of the plot in this regime

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY / ON FUEL CELLS



$R_{e^-}^x$: Electrical resistance

R_i^{elyte} : Ionic resistance

R_{CT} : Charge transfer resistance

C_{DL} : Double layer capacity (charge transfer processes across the double layer)

Z_{diff} : Diffusion-related impedance (also called Warburg resistance, W); it is characterized by a constant slope and $\theta = 45^\circ$.

Sometimes a Constant Phase Element, Z_{CPE} , is used to describe capacitive effects which have a strong non-ideal behaviour:

$$Z_{CPE} = 1 / \left((j\omega)^\beta Q \right)$$

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY / ON FUEL CELLS

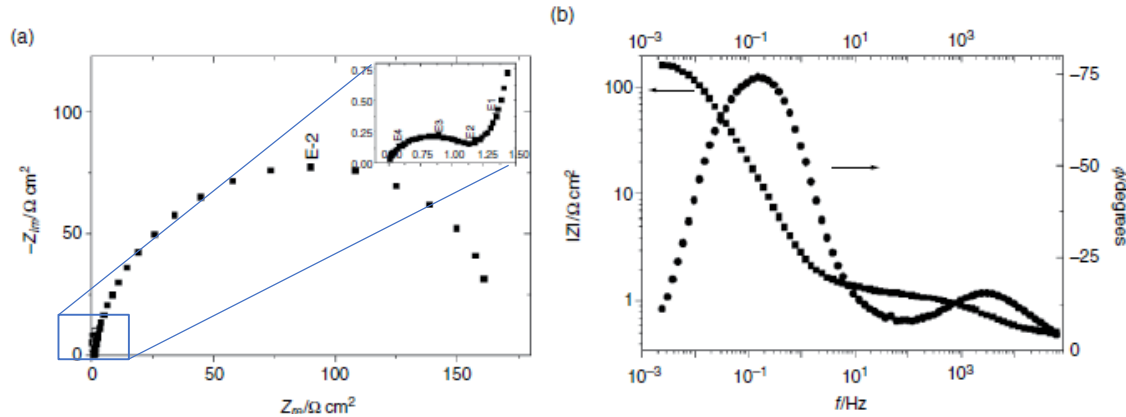


Figure 3.9 (a) Nyquist plot of a practical SOFC anode in 97% CH₄ and 3% H₂O, at 932°C. *Inset*: Zoom at frequencies higher than 1 Hz. (b) Corresponding Bode plots. (Source: Kelaidopoulou, A, Siddle, A, Dicks, AL, Kaiser, A and Irvine, JTS, 2001, Anodic behaviour of Y_{0.20}Ti_{0.18}Zr_{0.62}O_{1.90} towards hydrogen electro-oxidation in a high temperature solid oxide fuel cell, *Fuel Cells*, vol 1(3–4), pp. 226–232.)

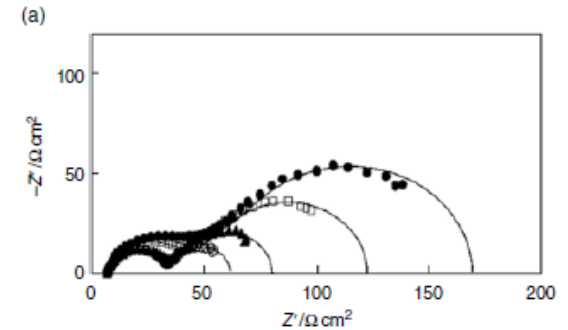


Figure 3.10 (a) Effect of overpotential on impedance plots for Nafion 117. Applied DC potential: (○) 0.775 V, (▲) 0.75 V, (◻) 0.725 V and (◊) 0.70 V. Temperature 303 K and oxygen pressure 207 kPa. Solid lines represent fits of the equivalent circuits. (b) Typical equivalent circuit of PEMFC for ORR at Pt/Nafion

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY / ON FUEL CELLS

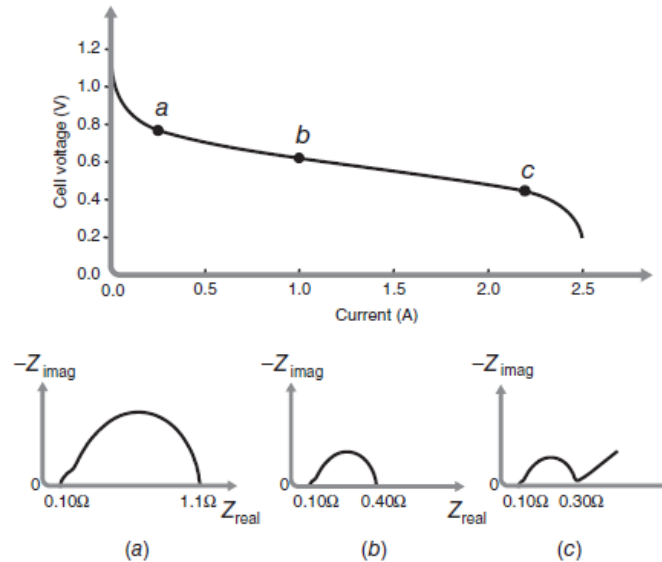


Figure 7.14. EIS characterization of a fuel cell requires impedance measurements at several different points along an i - V curve. The impedance response will change depending on the operating voltage. (a) At low current, the activation kinetics dominate and R_f is large, while the mass transport effects can be neglected. (b) At intermediate current (higher activation overvoltages), the activation loops decrease since R_f decreases with increasing η_{act} . (Refer to Equation 7.15.) (c) At high current, the activation loops may continue to decrease, but the mass transport effects begin to intercede, resulting in the diagonal Warburg response at low frequency.

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY / ON FUEL CELLS

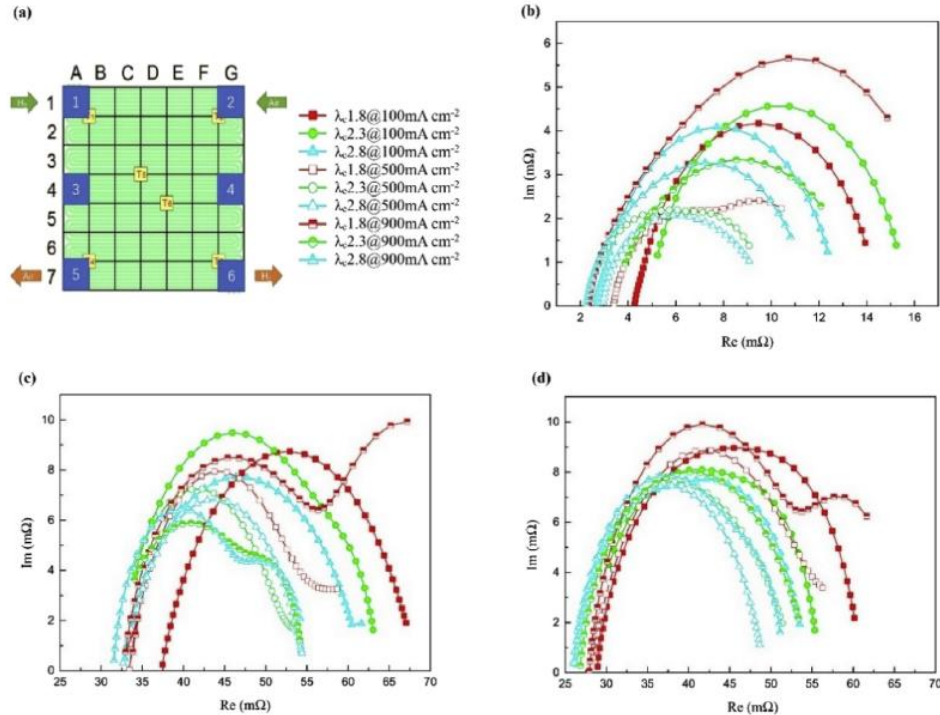


Fig. 5. (a) Distribution of the six special segments of the print circuit board; (b) Nyquist plot of the EIS results from the entire cell; (c) Nyquist plot of the local EIS results of Seg. 2 (cathode inlet); (d) Nyquist plot of the local EIS results of Seg. 5 (cathode outlet) [140]. Reproduced with permission from Ref. [140], Copyright 2019, Elsevier.

Z. Tang *et al.*, Journal of Power Sources 468 (2020) 228361

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY / ON FUEL CELLS

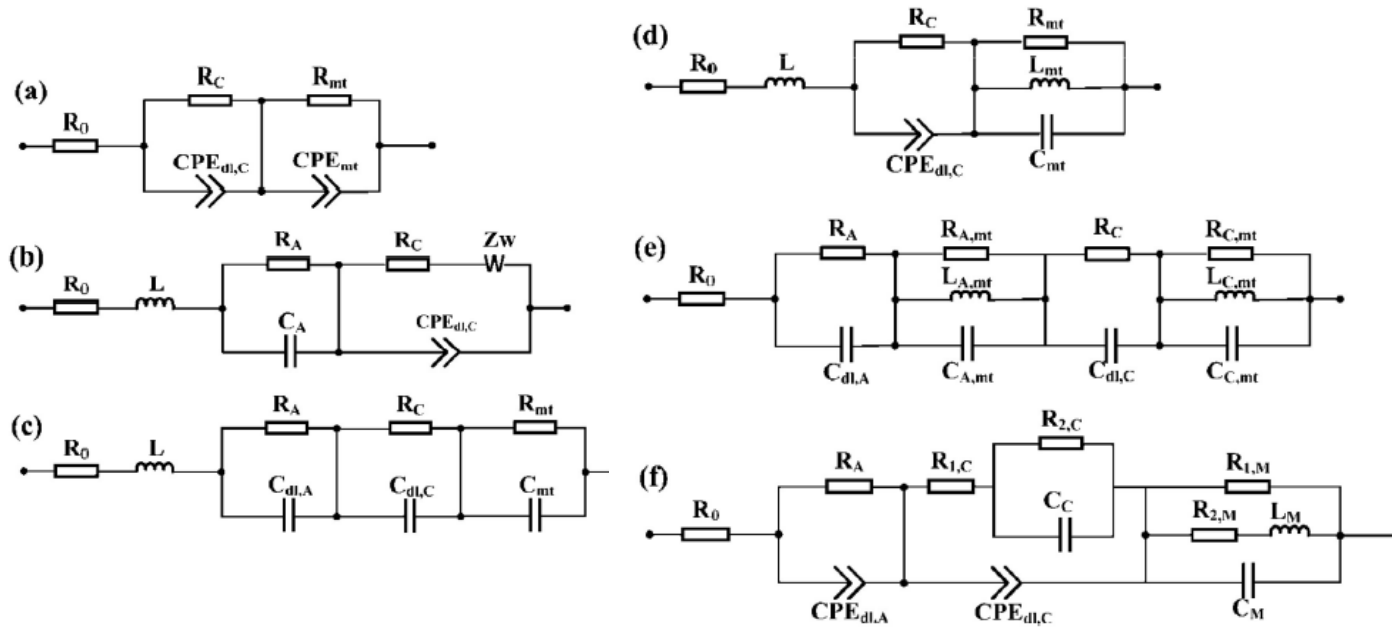
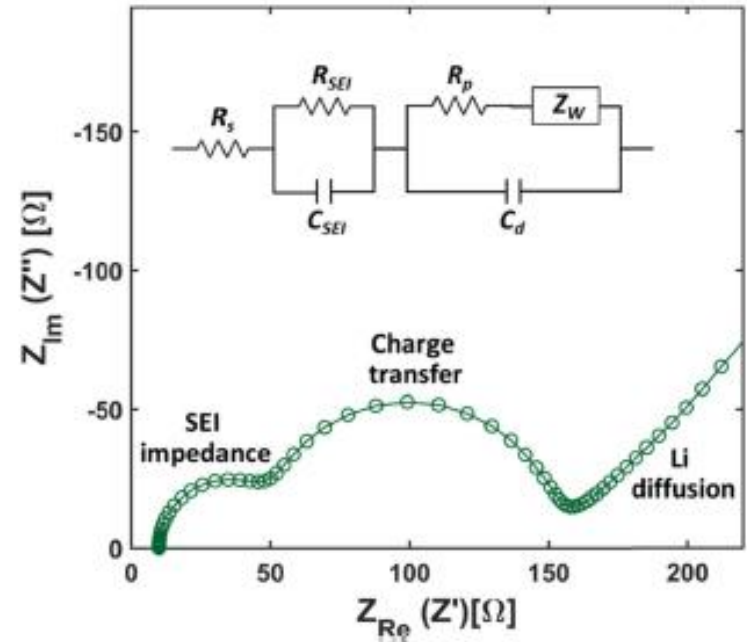


Fig. 2. Typical ECMs used to interpret the EIS data of PEMFCs under various conditions. (a) A 2 kW PEMFC stack [35], reproduced with permission from Ref. [35], Copyright 2007, Elsevier; (b) SO_2 contamination effects on ORR [36], reproduced with permission from Ref. [36], Copyright 2012, The Electrochemical Society; (c) electrode composition [37], reproduced with permission from Ref. [37], Copyright 2008, Elsevier; (d) water failure [38], reproduced with permission from Refs. [38], Copyright 2019, Elsevier; (e) inductive phenomena at LF [39] and (f) an ECM deduced from a complete process model [25,40], reproduced with permission from Ref. [25], Copyright 2016, Elsevier.

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY / ON BATTERIES

In principle, as performed in frequency domain, EIS allows to carry out a de-convoluted analysis of the different phenomena taking place in a battery during operation. As an example:

- Ionic conductivity and relative permittivity of an electrolyte can be extracted from the solution resistance (R_s) and the double layer capacitance (C_d).
- Double layer capacitance is also used to model and characterize the double layer formation at the electrodes interface
- By means of the polarization resistance (R_p) the evolution charge transfer processes associated at the electrode/electrolyte interface can be investigated.
- Diffusion processes are represented by means of Constant Phase Elements (also known as Warburg diffusion elements).

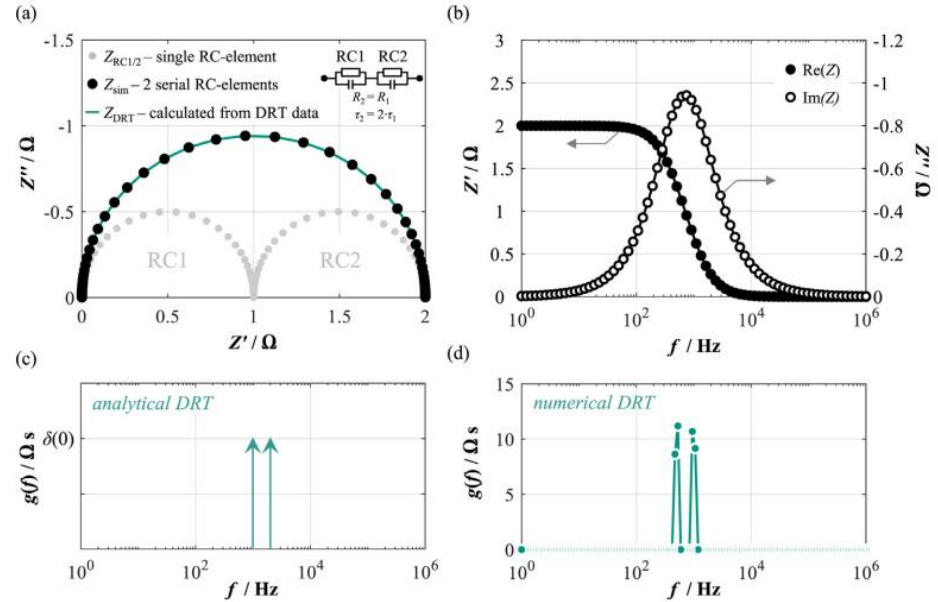
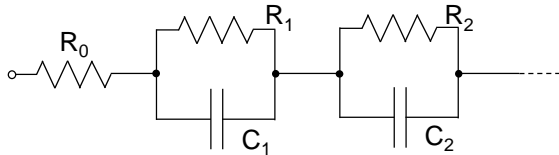


ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY / DRT

Once of the main issues in EIS is related to the difficulty in finding the most suitable model to be used for data analysis, which is not always straightforward.

In this framework, Distribution of Relaxation Times analysis was developed, to better identify the relaxation time constants present in the system under investigation, by in turning the frequency dependence of the impedance data into a distribution of the time constants. To do this, a function composed by a finite number of RC-parallel elements is used:

$$Z(\omega) = \sum_{k=1}^N \frac{R_k}{1+i\omega\tau_k} \quad \tau_k = R_k C_k$$



https://www.biologic.net/wp-content/uploads/2019/08/battery-eis-distribution-of-relaxation-times-drt_electrochemistry-an60.pdf

S. Dierickx, A. Weber and E. Ivers-Tiffée / Electrochimica Acta 355 (2020) 136764

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY / DRT

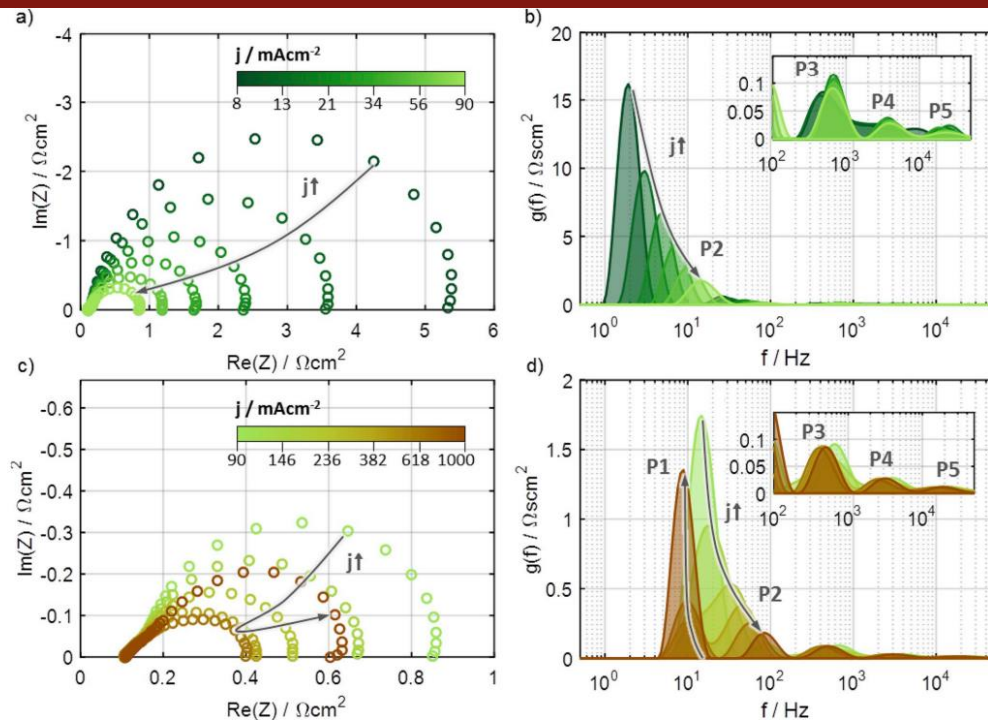


Fig. 1. Impedance spectra (a,c) and calculated DRTs (b,d) as a function of current density and with separation of individual polarization contributions ($T = 80\text{ }^{\circ}\text{C}$, 70% R.H., and H_2/air).

Table 1

Process assignment of identified polarization contributions to the underlying physical mechanisms.

Process	Dependencies	Relaxation frequency	Physical origin
P1	j , $p\text{O}_{2,\text{cat}}$, R.H.	2–10 Hz	gas diffusion of oxygen in GDL and CCL
P2	j , $p\text{O}_{2,\text{cat}}$ (strong), R.H. (low)	2–200 Hz	charge transfer kinetics at the cathode (ORR)
P3 – P5	R.H.	300 Hz–30 kHz	proton conduction in the ionomer of the cathode catalyst layer (subordinate anode processes)

OUTLOOK / *IN SITU* ELECTROCHEMICAL CHARACTERIZATION

Polarization curve

Cyclic Voltammetry

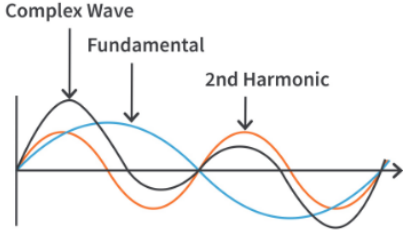
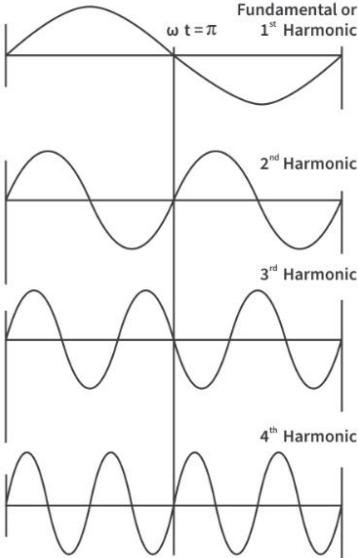
Linear Sweep Voltammetry

Tafel plots

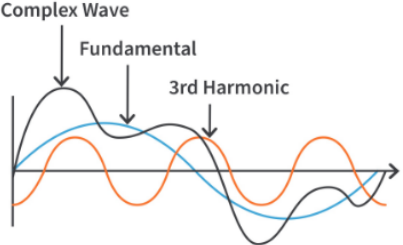
Electrochemical Impedance Spectroscopy

Total Harmonic Distortion

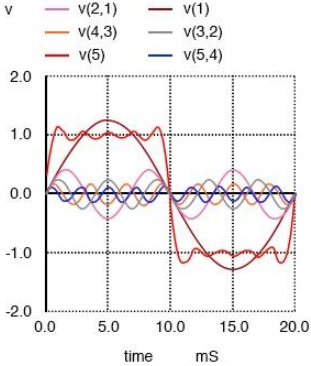
TOTAL HARMONIC DISTORTION



This waveform contains a 2nd harmonic.



This waveform contains a 3rd harmonic.



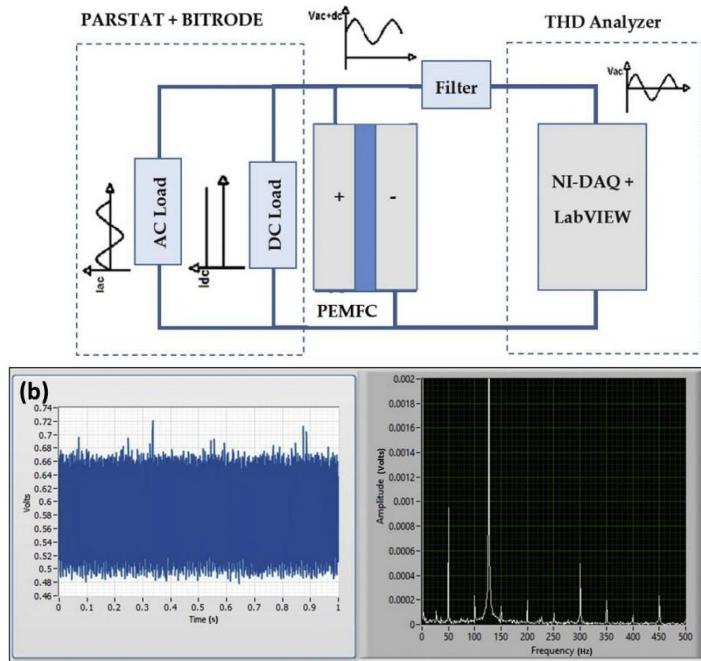
TOTAL HARMONIC DISTORTION

Total harmonic distortion, is a measurement of the level of harmonic distortion present in power systems. It can be related to either current harmonics or voltage harmonics, and it is defined as the ratio of the RMS value of all harmonics to the RMS value of the fundamental component times 100%; the DC component is neglected.

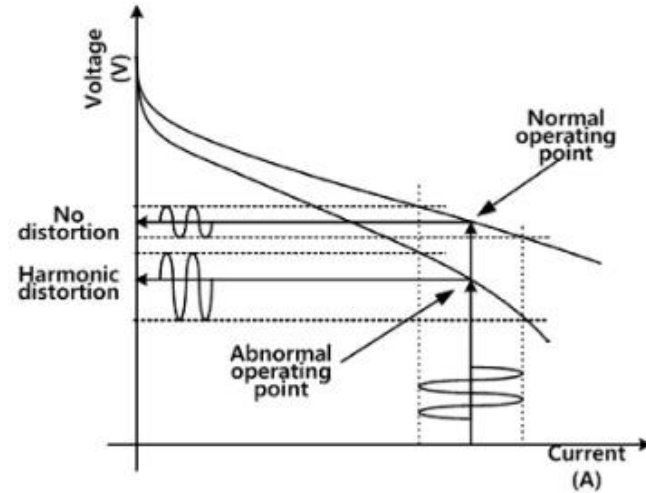
$$THD_V = \frac{\sqrt{\sum_{k=2}^N V_k^2}}{V_1}$$

where V_k is the RMS voltage of the k th harmonic and $k = 1$ is the order of the fundamental component.

TOTAL HARMONIC DISTORTION

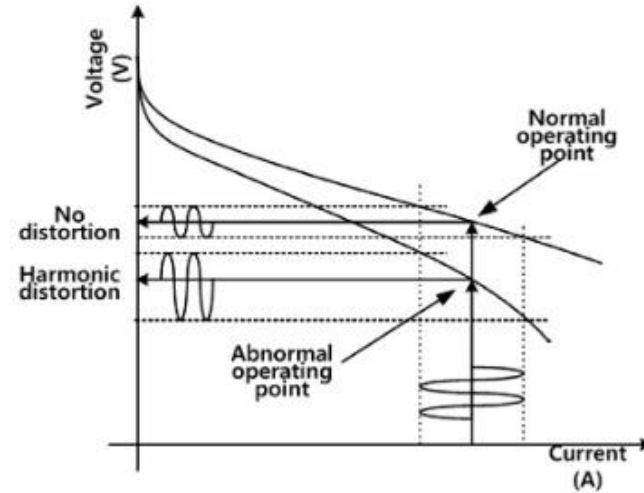
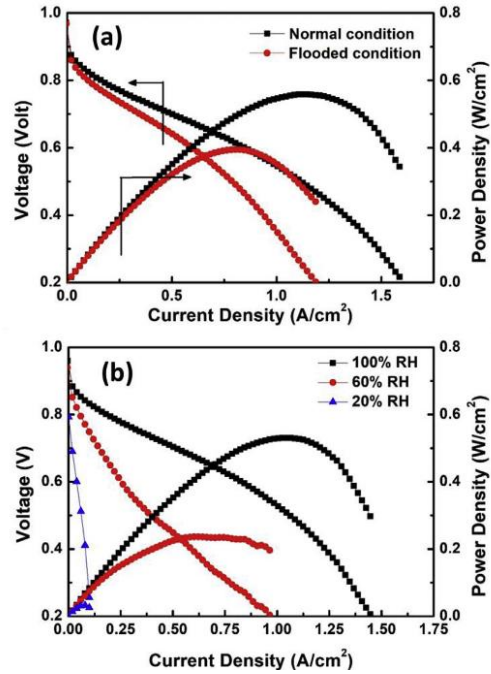


N.J. Steffy et al. Journal of Power Sources 404 (2018) 81–88



E. Ramschak et al. / Journal of Power Sources 157 (2006) 837–840

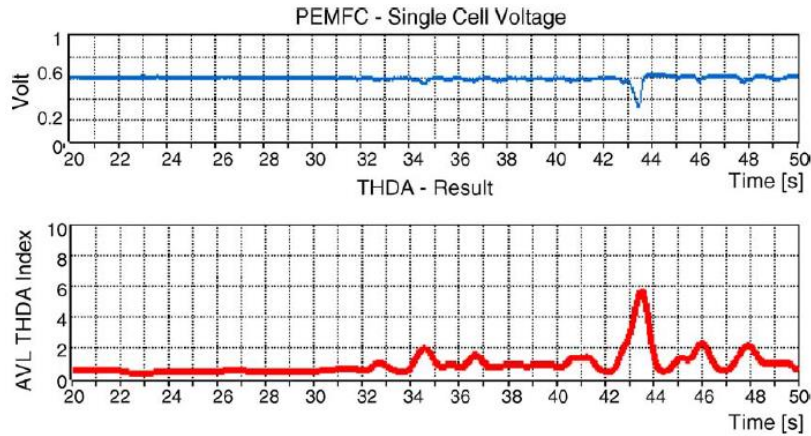
TOTAL HARMONIC DISTORTION



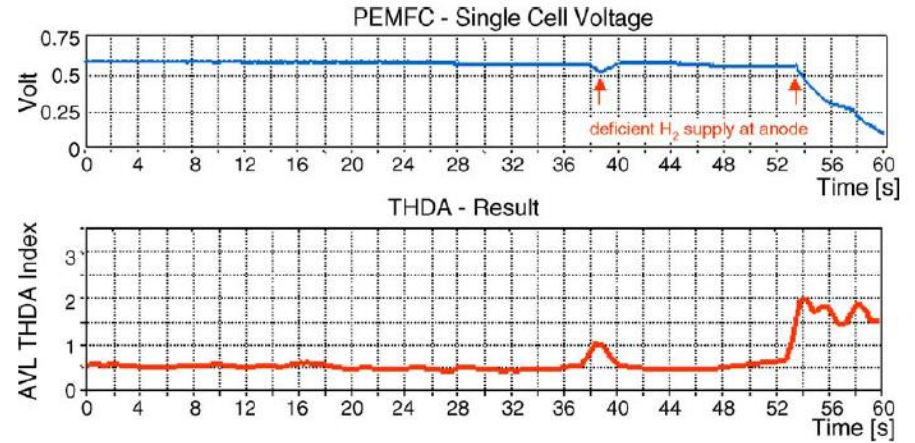
E. Ramschak et al. / Journal of Power Sources 157 (2006) 837–840

TOTAL HARMONIC DISTORTION

Air Starvation



H2 supply deficiency



OUTLOOK

Electrochemical Characterization Techniques (In Situ)

These techniques use the electrochemical variables of voltage, current, and time to characterize the performance under operating conditions of either a single component or the full assembly of an electrochemical device.

Ex Situ / In Situ Complementary Characterization Techniques

These techniques characterize the detailed structure or properties of the individual components composing the fuel cell, but generally only components removed from the device in an unassembled, non-functional form.

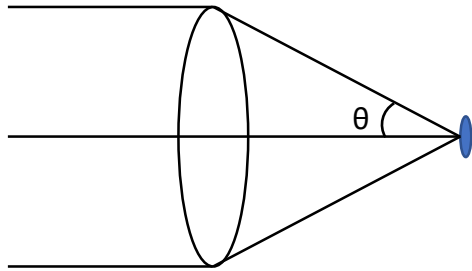
Advanced Characterization Techniques (*Ex Situ / In situ*)

These techniques characterize the detailed structure or properties of the individual components inside the device.

ELECTRON MICROSCOPY

Starting from the discoveries of Ernst Abbe in 1873 about optics, the so called “The Abbe diffraction limit” could be formulated, stating that the smallest spot you can focus down to is related to the wavelength of used radiation as:

$$d = \frac{\lambda}{2 n \sin \theta} \rightarrow d \propto \lambda \rightarrow d \geq \frac{\lambda}{2}$$



According to wave/particle duality every particle can be considered either a particle or a wave. In 1925 Louis de Broglie assumed that for particles are valid the same relations which were used for the photon, thus defining:

$$E = h\nu \quad \lambda = c/\nu \quad E = \frac{hc}{\lambda} = pc$$
$$\lambda_B = \frac{h}{p} \rightarrow \lambda_B \propto \frac{1}{E}$$

TRANSMISSION ELECTRON MICROSCOPY

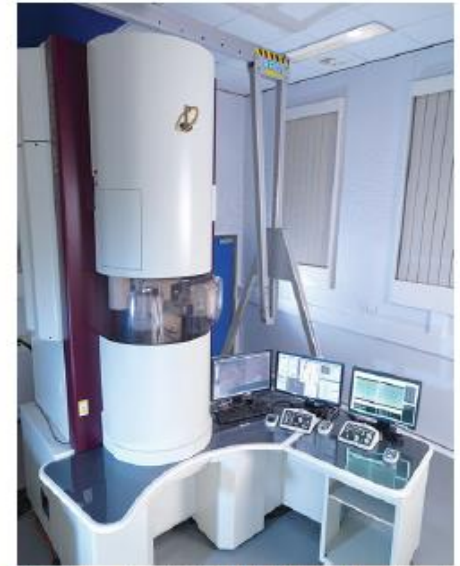
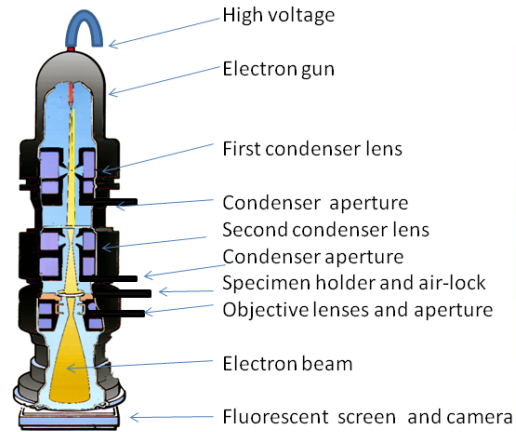
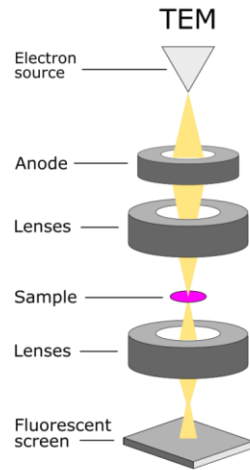
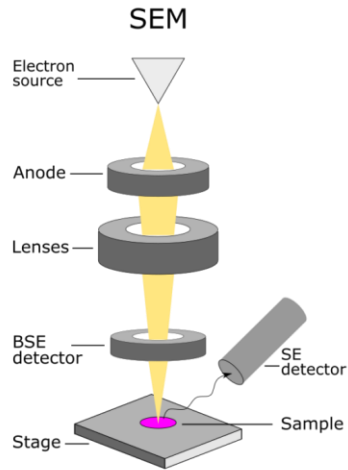
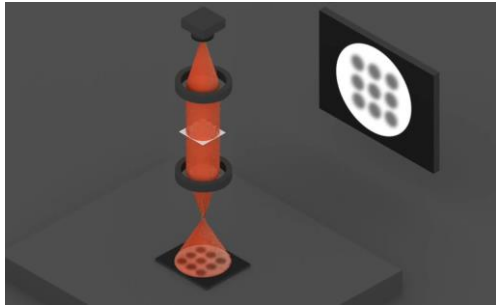


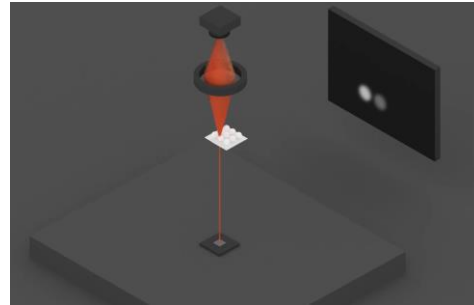
Fig. 1.1 A modern 30–300 kV HRTEM fitted with a cold field-emission gun, probe- and image-forming aberration correctors, and a range of digital detectors for HRTEM and STEM (scanning transmission electron microscopy) and configured for full remote operation

<https://anapath.ch/electron-microscopy-2/>

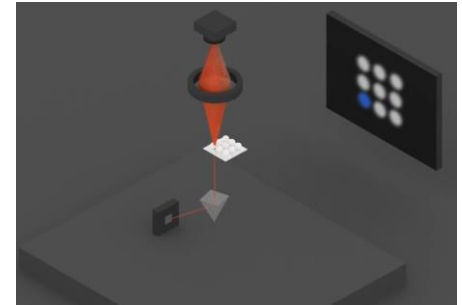
TRANSMISSION ELECTRON MICROSCOPY



transmission

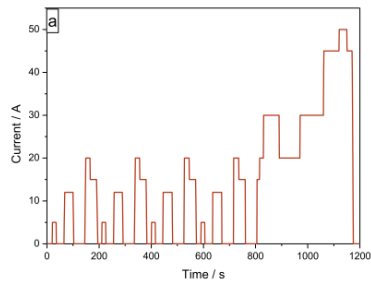
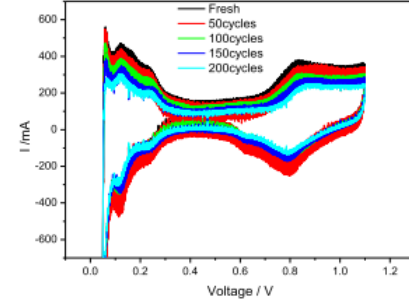
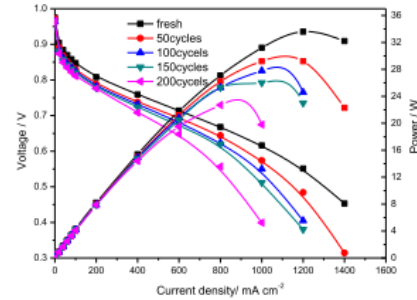
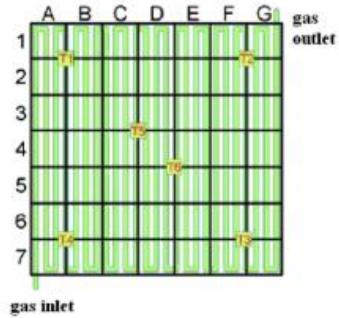
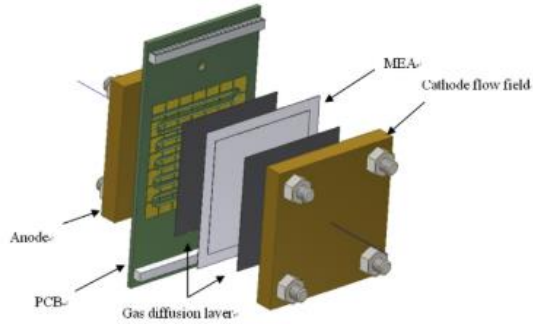


scanning

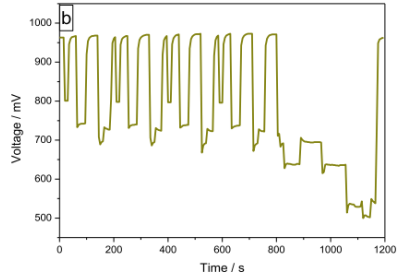


EELS

TRANSMISSION ELECTRON MICROSCOPY FOR FUEL CELLS AND BATTERIES

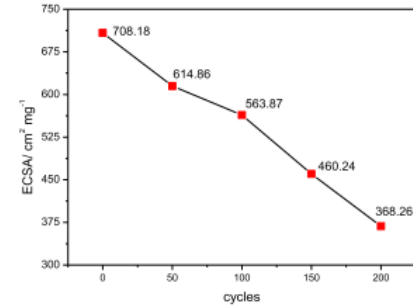


(a)



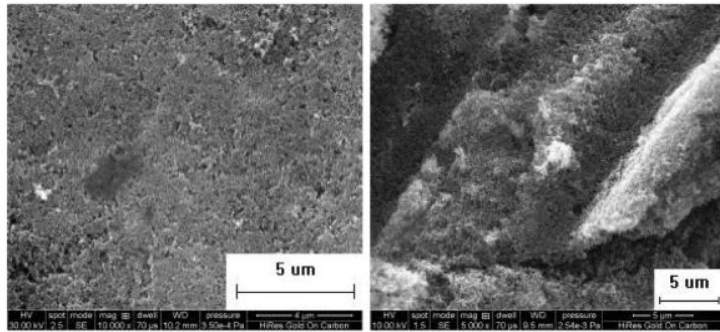
(b)

Fig. 2 – Evolution of (a) current in a simulating driving cycle and (b) response voltage in one cycle.



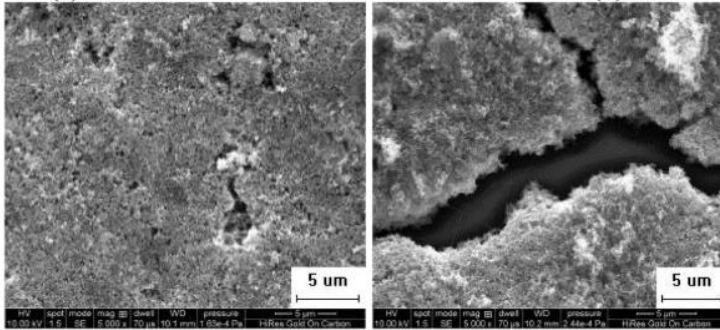
Shan, Int. J. Hydrogen Energy, 2016, 41, 7, 4239-4250

TRANSMISSION ELECTRON MICROSCOPY FOR FUEL CELLS AND BATTERIES



(a) fresh

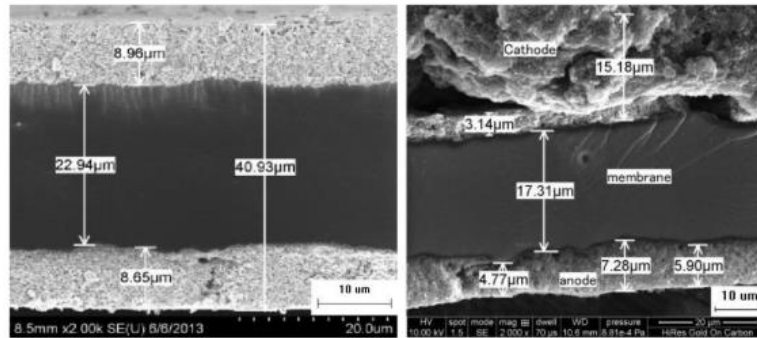
(b) inlet



(c) middle

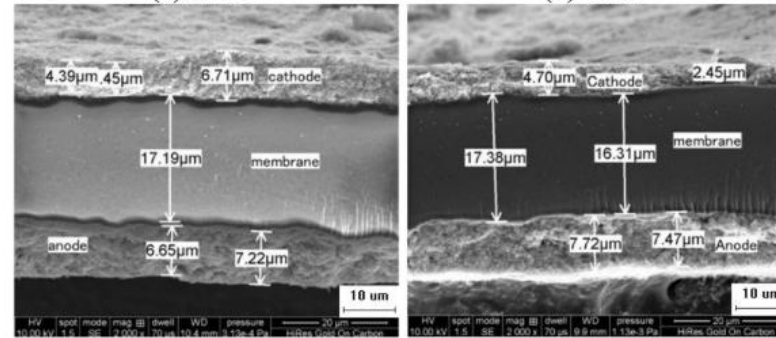
(d) outlet

Fig. 10 – Scanning electron micrograph of the surface layer of cathode catalyst.



(a) fresh

(b) inlet



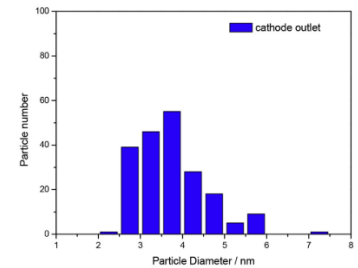
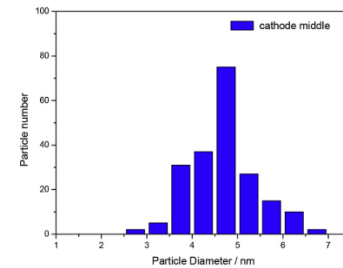
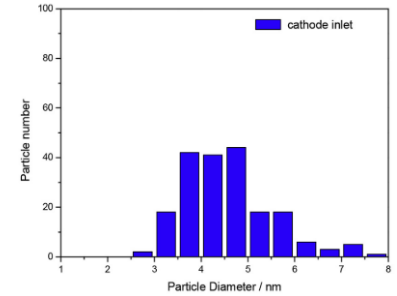
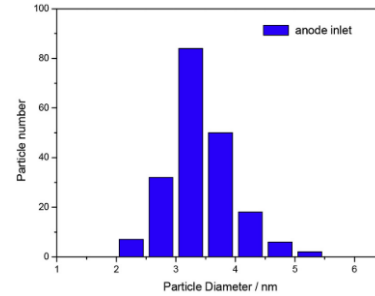
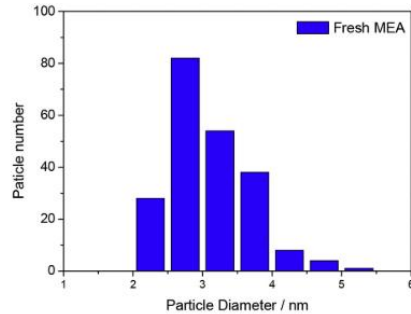
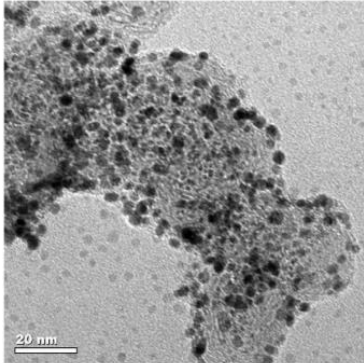
(c) middle

(d) outlet

Fig. 11 – Cross-section of MEA morphology.

Shan, Int. J. Hydrogen Energy, 2016, 41, 7, 4239-4250

TRANSMISSION ELECTRON MICROSCOPY FOR FUEL CELLS AND BATTERIES



Shan, Int. J. Hydrogen Energy, 2016, 41, 7, 4239-4250

OVERVIEW OF CHARACTERIZATION TECHNIQUES

Electrochemical Characterization Techniques (In Situ)

These techniques use the electrochemical variables of voltage, current, and time to characterize the performance under operating conditions of either a single component or the full assembly of an electrochemical device.

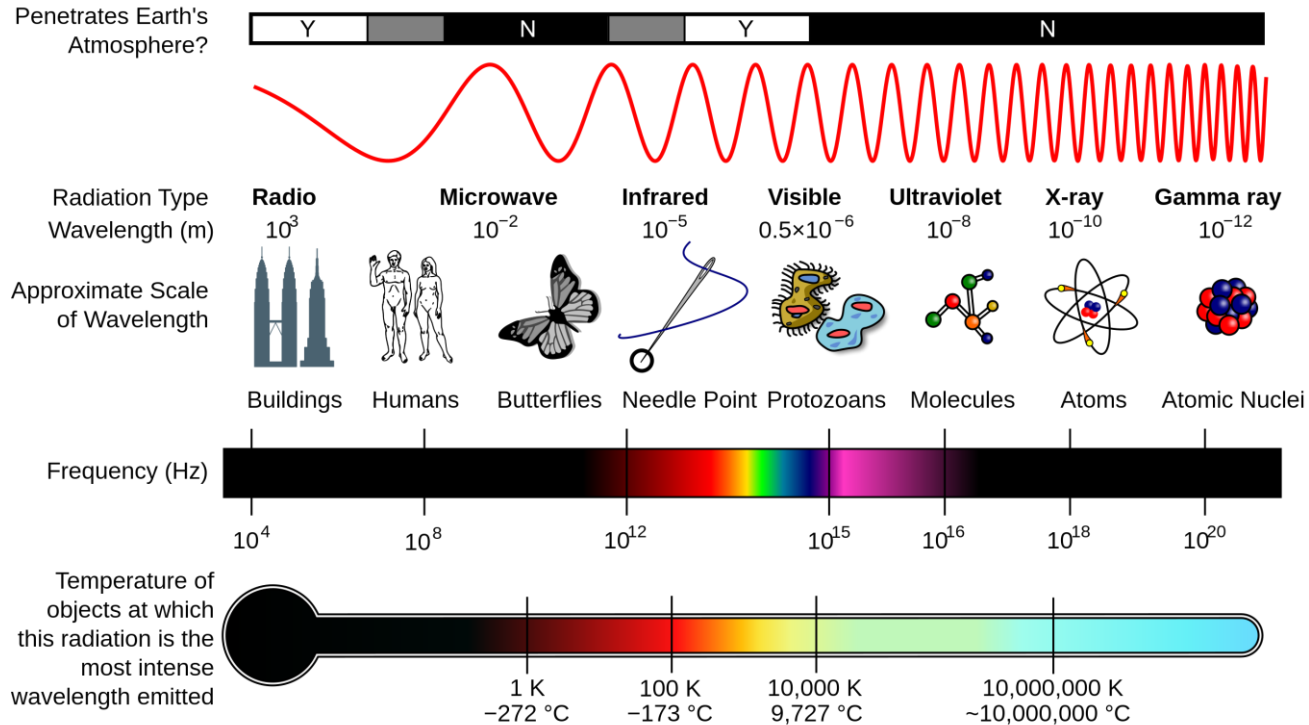
Ex Situ / In Situ Complementary Characterization Techniques

These techniques characterize the detailed structure or properties of the individual components composing the fuel cell, but generally only components removed from the device in an unassembled, non-functional form.

Advanced Characterization Techniques (*Ex Situ / In situ*)

These techniques characterize the detailed structure or properties of the individual components inside the device.

X-RAYS / THE ELECTROMAGNETIC SPECTRUM

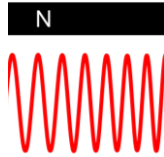


X-Rays can be seen as the electromagnetic radiation in the region of an Angstrom (10^{-10} m). They can be

$$E = \frac{hc}{\lambda}$$

X-RAYS

Penetrates Earth's Atmosphere?



Radiation Type
Wavelength (m)

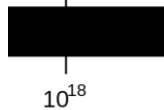
X-ray
 10^{-10}

Approximate Scale
of Wavelength

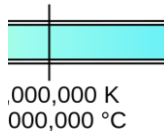


Atoms

Frequency (Hz)



Temperature of
objects at which
this radiation is the
most intense
wavelength emitted

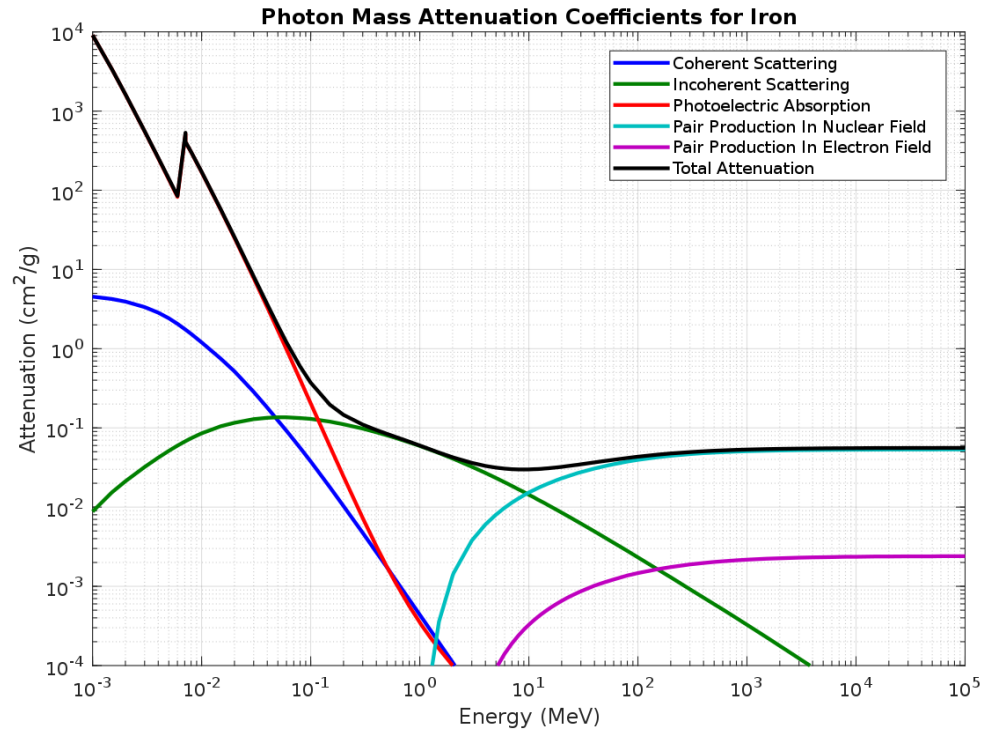


X-Rays are the electromagnetic radiation in the region of an Angstrom (10^{-10}m), more precisely they cover the range from 10^{-8} to 10^{-12} m.

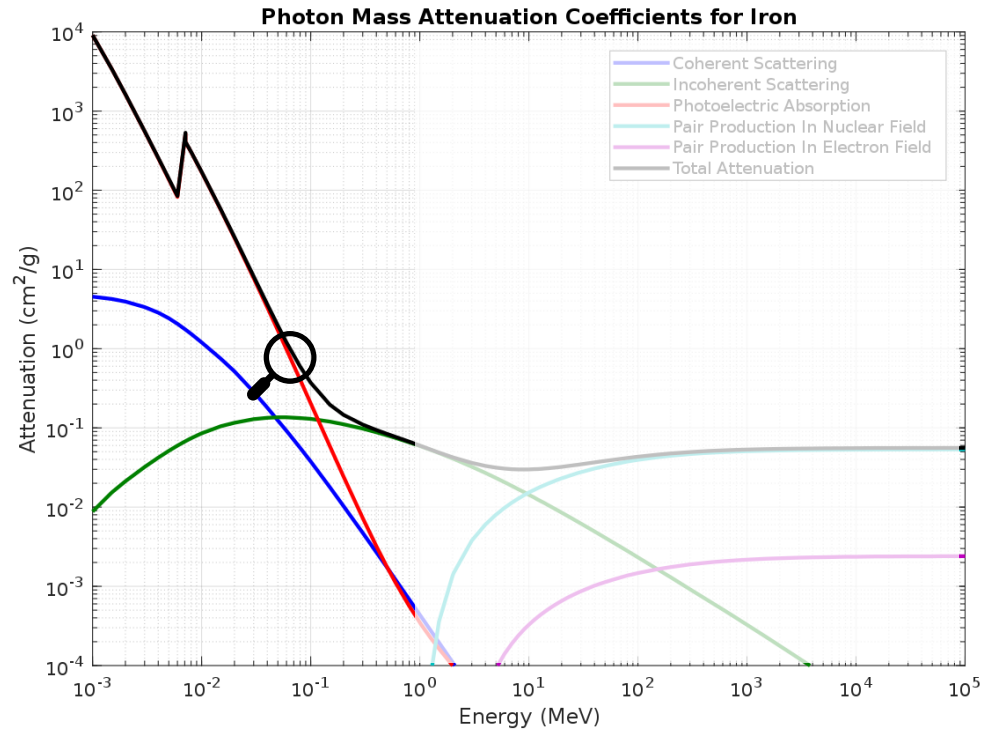
They can be described in function of their wavelength or in function of their energy: usually at wavelengths bigger than 1 \AA the Soft X-Ray region is defined, while at wavelengths of 1 \AA or below, the Hard X-Ray can be found.

$$E = \frac{hc}{\lambda} \rightarrow E(\text{keV}) = \frac{12398}{\lambda(\text{\AA})}$$

RADIATION – MATTER INTERACTION

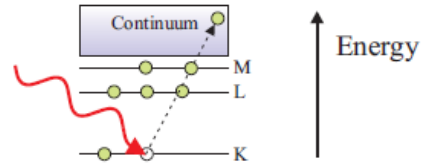


RADIATION – MATTER INTERACTION

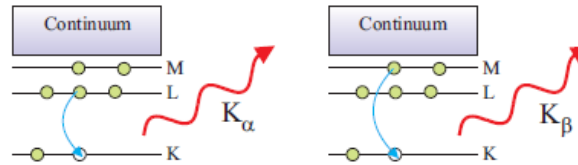


RADIATION – MATTER INTERACTION / X-RAY ABSORPTION

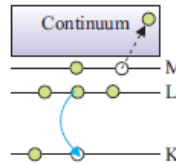
(a) Photoelectric absorption



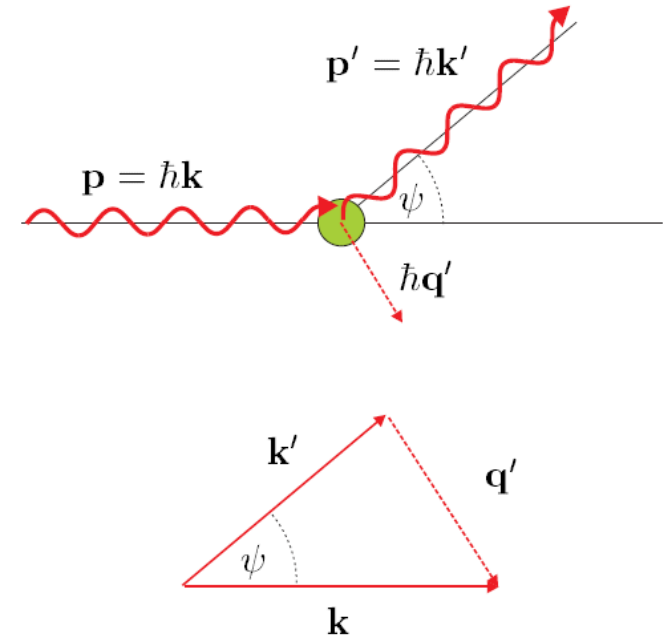
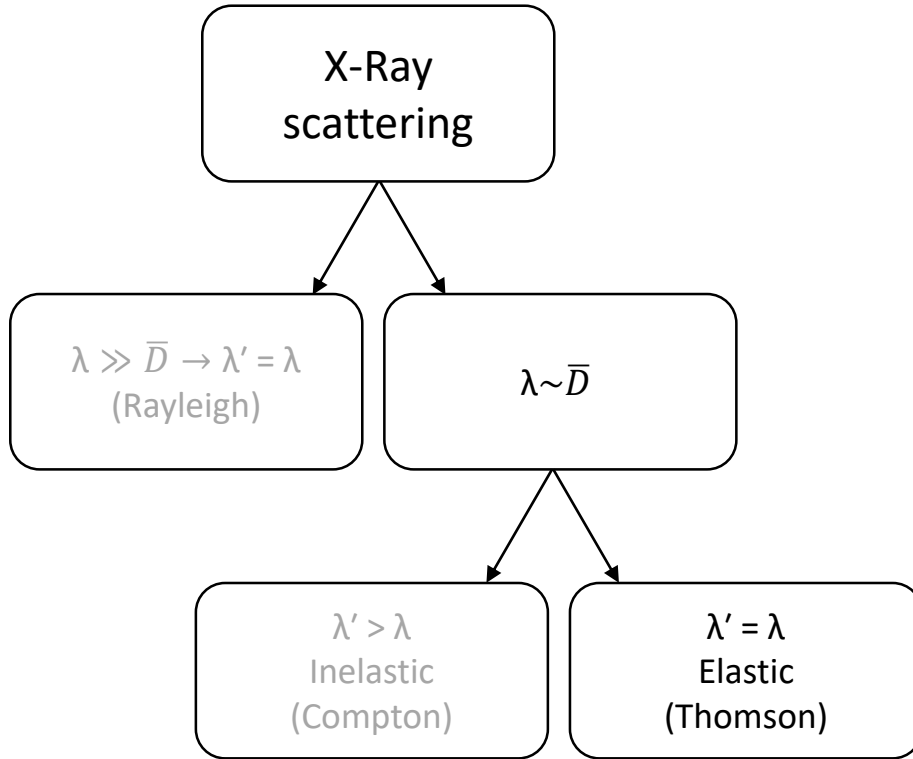
(b) Fluorescent X-ray emission



(c) Auger electron emission

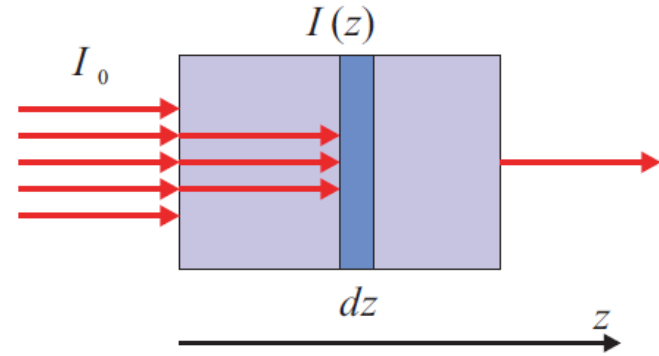
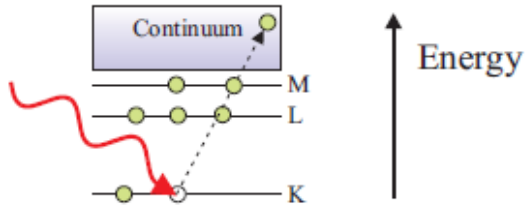


RADIATION – MATTER INTERACTION / X-RAY SCATTERING



X-RAY ABSORPTION

(a) Photoelectric absorption



$$-dI = I(z) \mu dz$$

$$\frac{dI}{I(z)} = -\mu dz$$

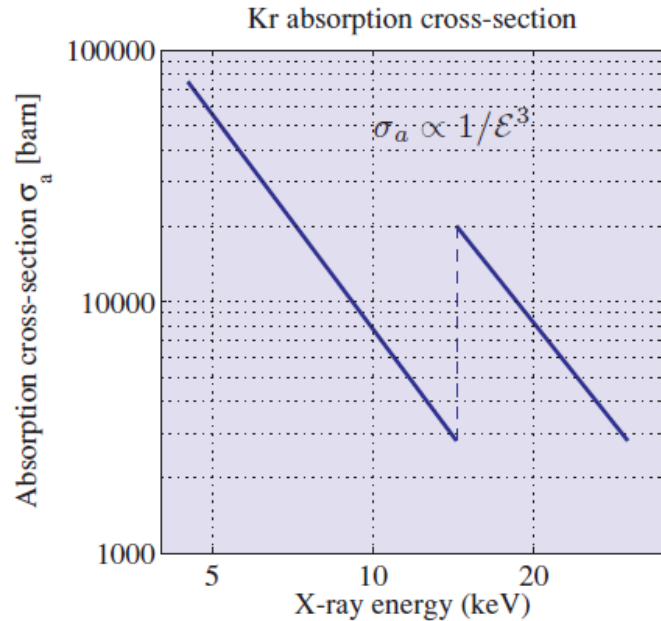
$$I(z) = I_0 e^{-\mu z}$$

X-RAY ABSORPTION / THE ABSORPTION COEFFICIENT

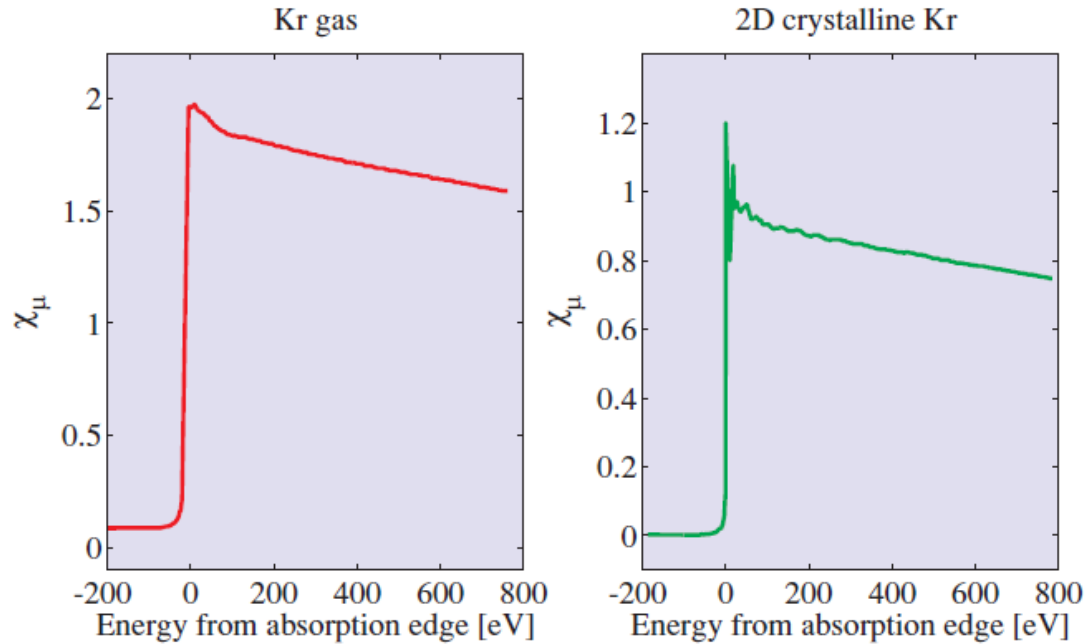
$$\mu = \rho_{at} \sigma_{at} = \left(\frac{\rho_m N_A}{M} \right) \sigma_a$$

For composite materials

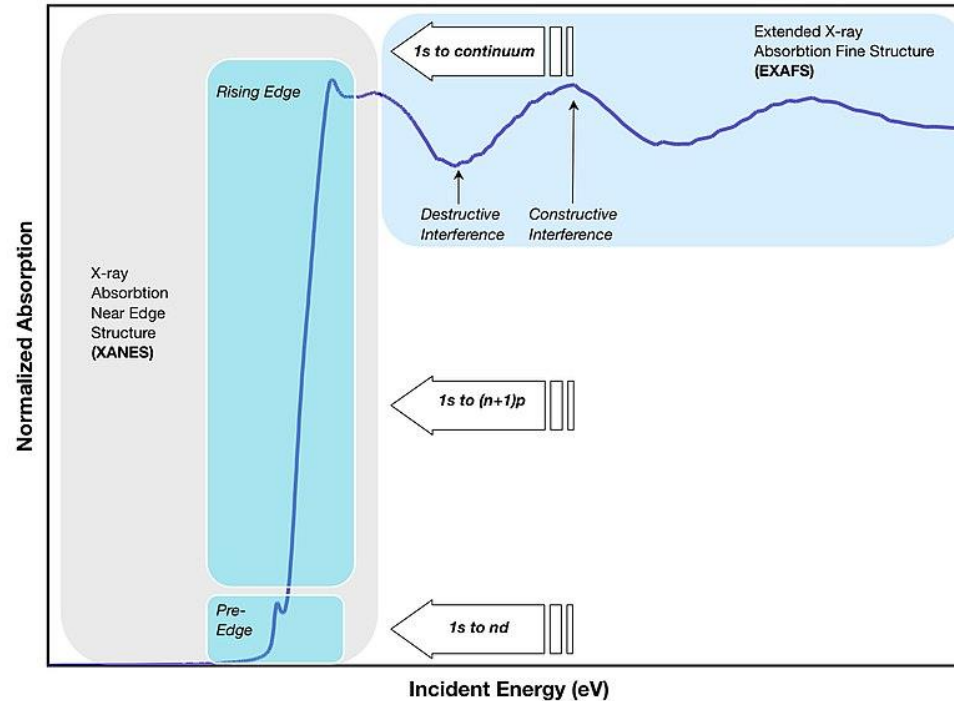
$$\mu = \sum_j \rho_{at,j} \sigma_{at,j}$$



X-RAY ABSORPTION / THE XAS SPECTRUM

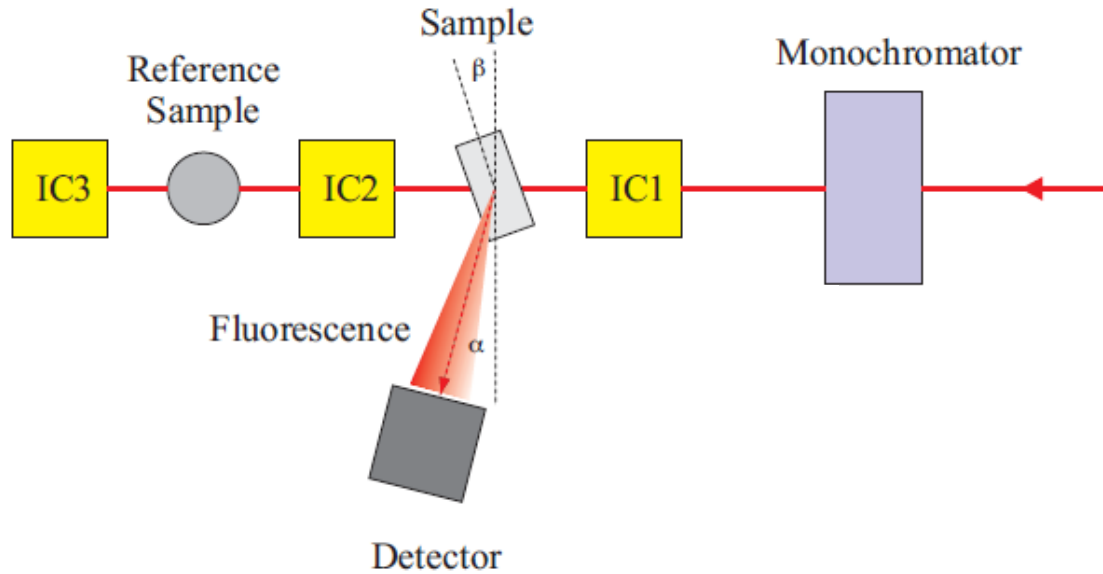


X-RAY ABSORPTION / THE XAS SPECTRUM

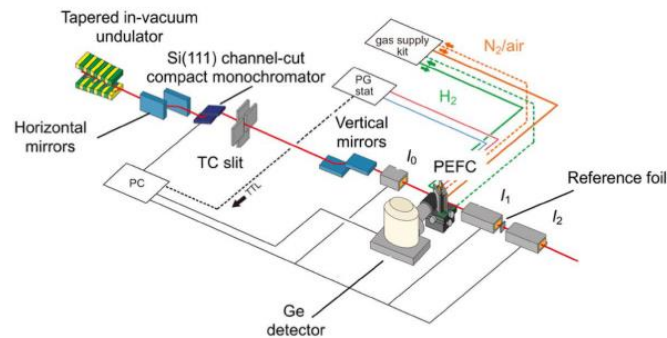
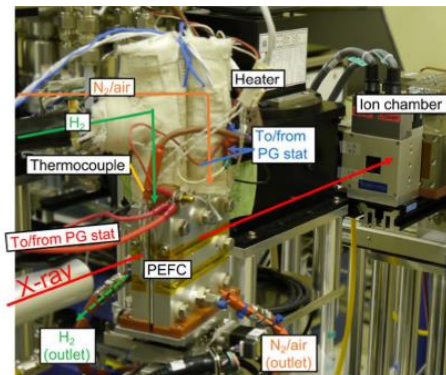
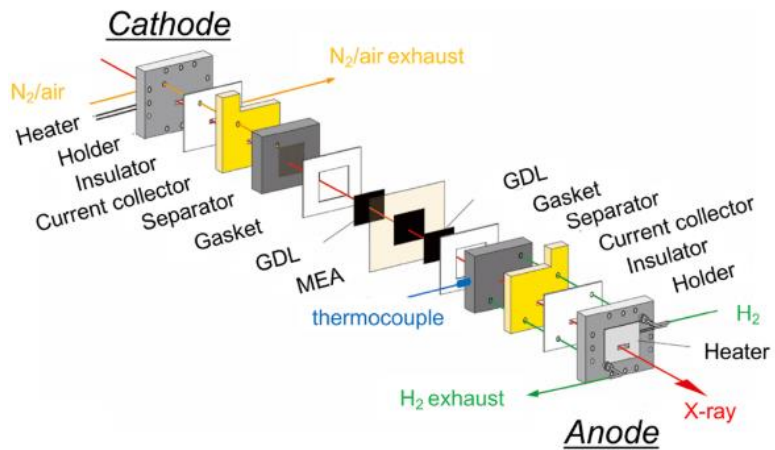


https://en.wikipedia.org/wiki/X-ray_absorption_spectroscopy

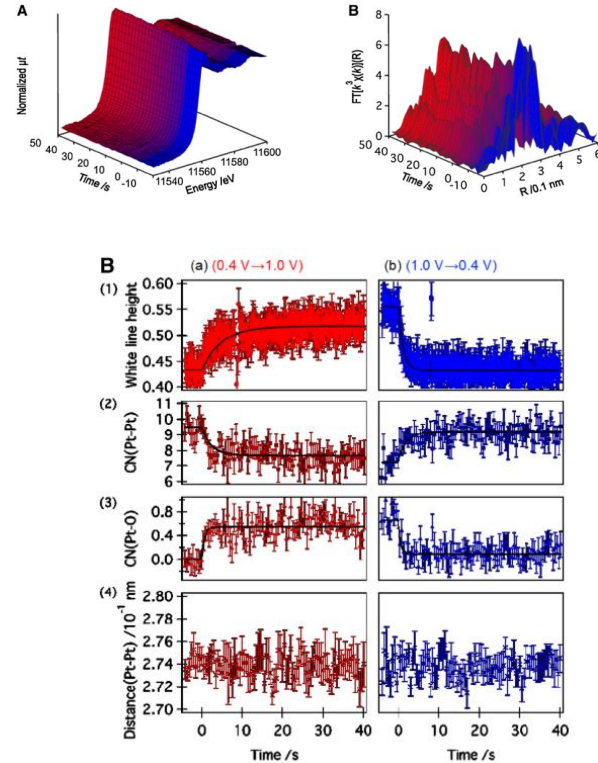
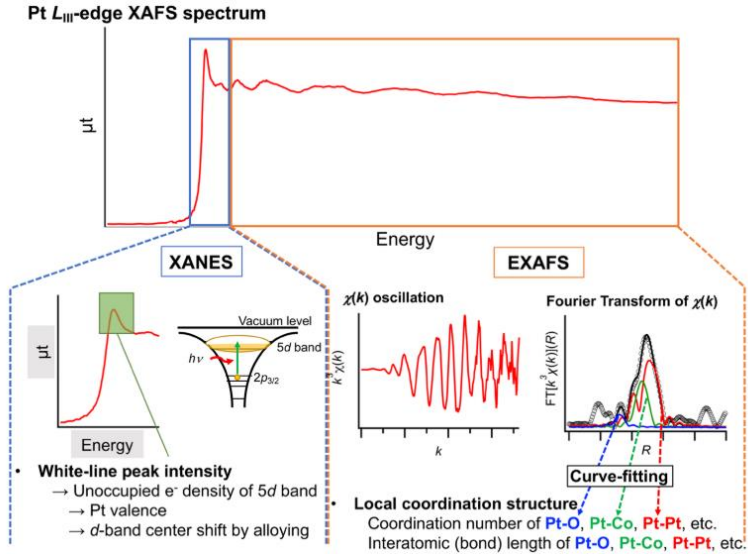
X-RAY ABSORPTION / THE SETUP



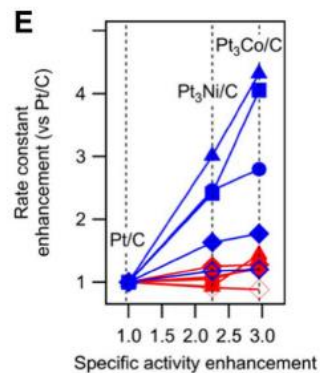
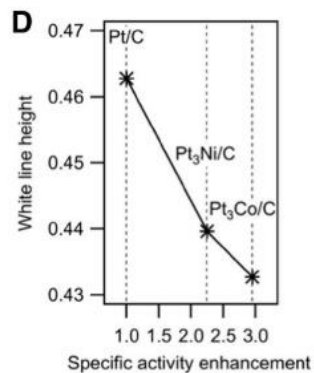
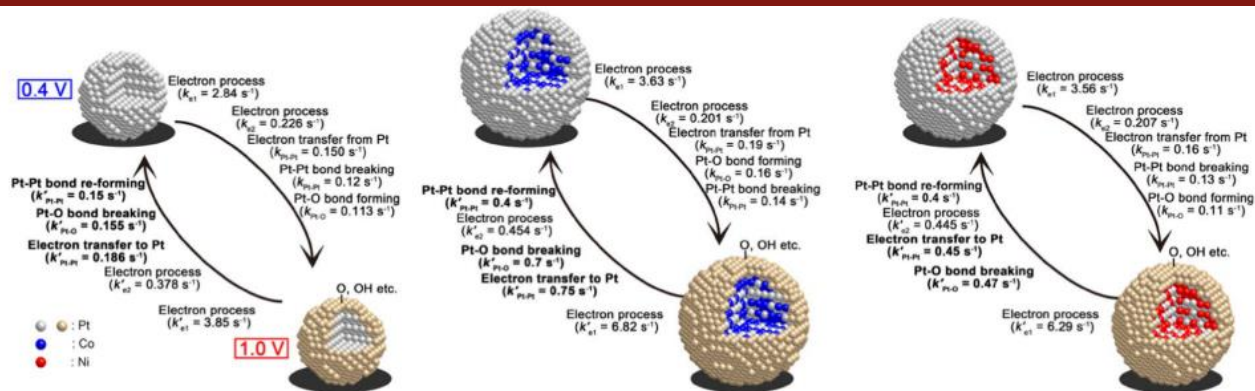
X-RAY ABSORPTION / CASE OF STUDY



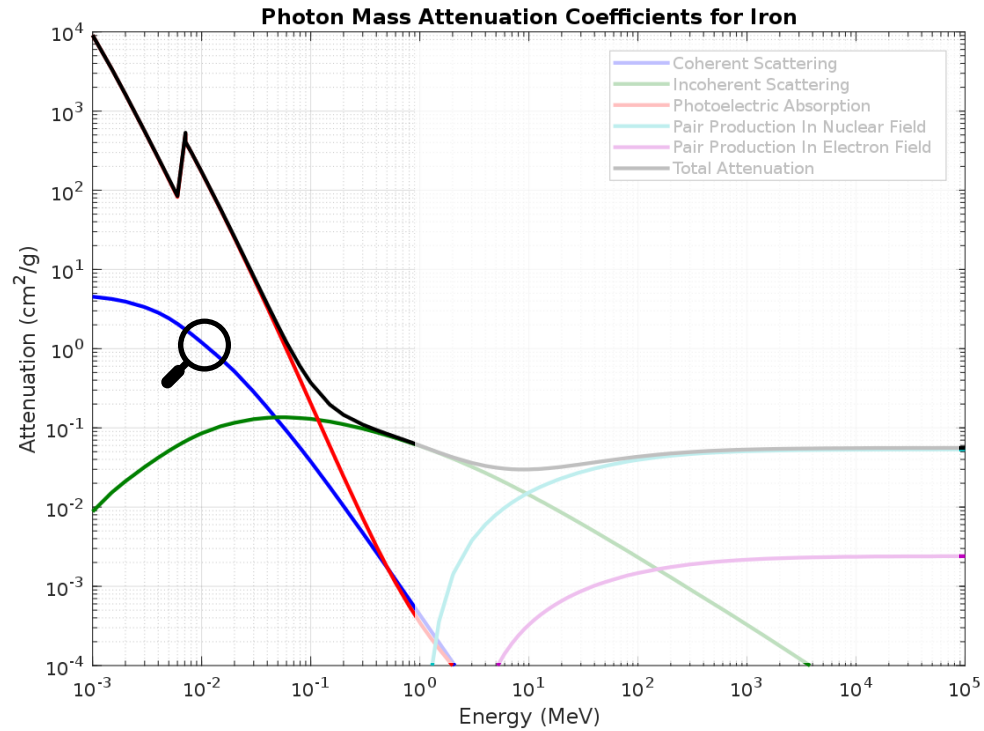
X-RAY ABSORPTION / CASE OF STUDY



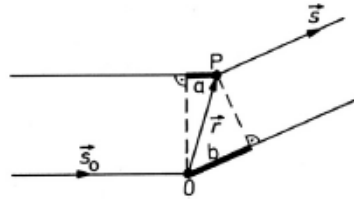
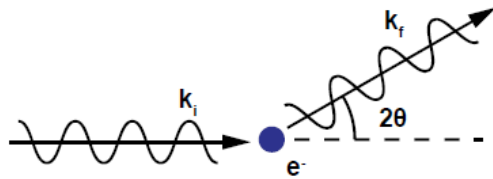
X-RAY ABSORPTION / CASE OF STUDY



RADIATION – MATTER INTERACTION



X-RAY SCATTERING

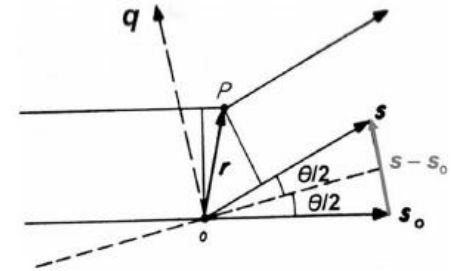


$$a = \vec{r} \cdot \vec{s}_0$$

$$b = \vec{r} \cdot \vec{s}$$

$$a - b = r s_0 - r s = r(s_0 - s)$$

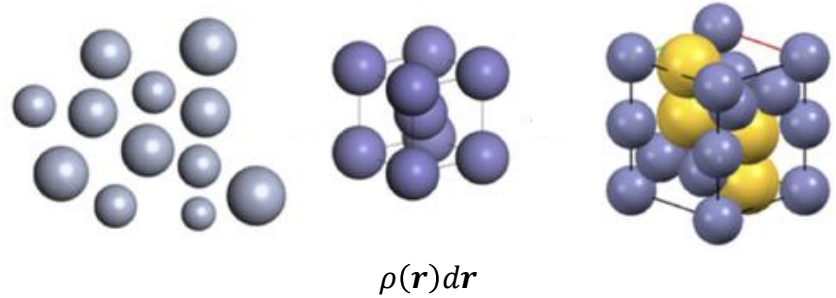
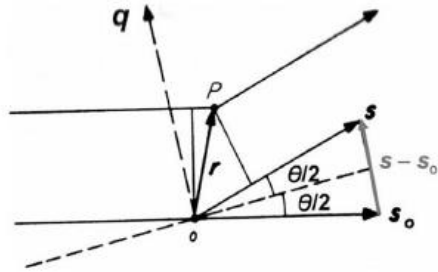
$$\varphi = -\frac{2\pi}{\lambda} r(s_0 - s) = -qr$$



$$q = -\frac{2\pi}{\lambda} (s_0 - s) \rightarrow q = k - k_0$$

$$q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$$

X-RAY SCATTERING



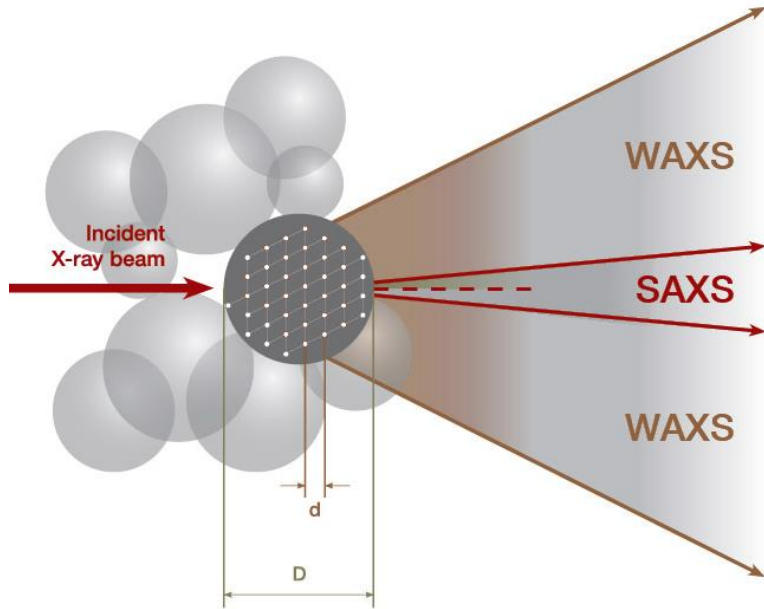
$$\mathbf{q} = -\frac{2\pi}{\lambda}(\mathbf{s}_0 - \mathbf{s}) \rightarrow \mathbf{q} = \mathbf{k} - \mathbf{k}_0$$

$$\varphi = -\mathbf{q}\mathbf{r}$$

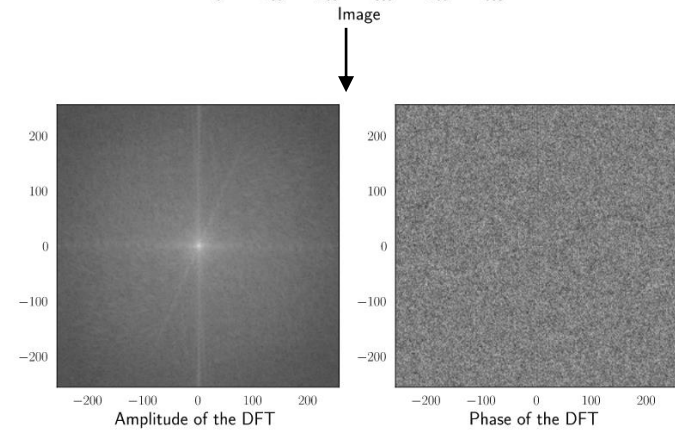
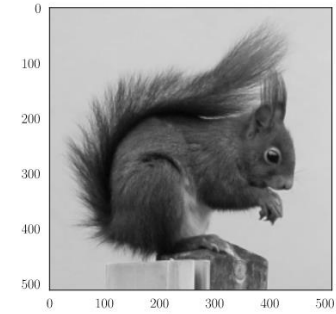
$$I(\mathbf{q}) = \int_V \rho(\mathbf{r})e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r}$$

Due to the similarity theorem of the Fourier transformation, we can call the space containing all position vectors \mathbf{r} the real space, and the space containing the vectors \mathbf{q} the reciprocal space.

X-RAY SCATTERING



<https://wiki.anton-paar.com/cn-cn/saxs-nanostructure-analysis/>



<https://vincmazet.github.io/bip/filtering/fourier.html>

X-RAY SCATTERING / THE FORM FACTOR

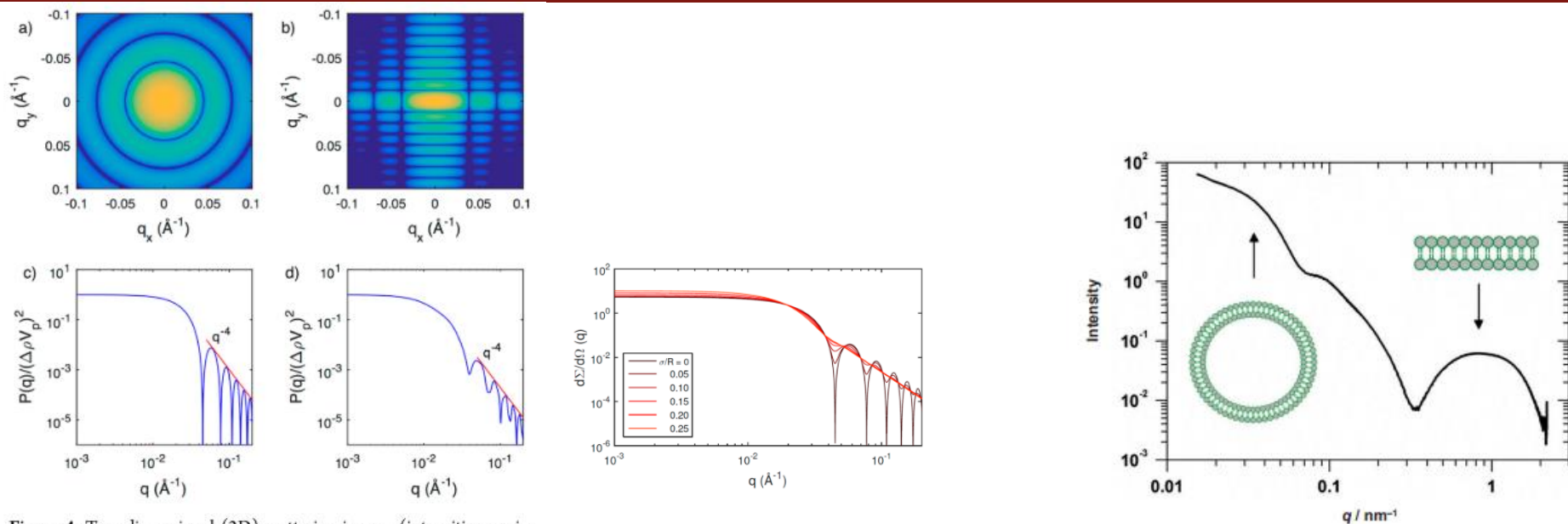


Figure 4. Two-dimensional (2D) scattering images (intensities are in log scale) of (a) sphere and (b) cylinder, where the axis of the cylinder is parallel to the y -axis. The 1D SAXS curves in (c) and (d) are the scatterings from randomly oriented spheres and cylinders, respectively. Intensities are normalized so that $P(0) = 1$. The radius of the sphere is 10 nm, and the radius and length of the cylinder are 10 and 50 nm, respectively.

Chem. Rev. 2016, 116, 18, 11128–11180

PTB-Mitteilungen 124 (2014), No. 3 / 4

X-RAY SCATTERING / THE STRUCTURE FACTOR

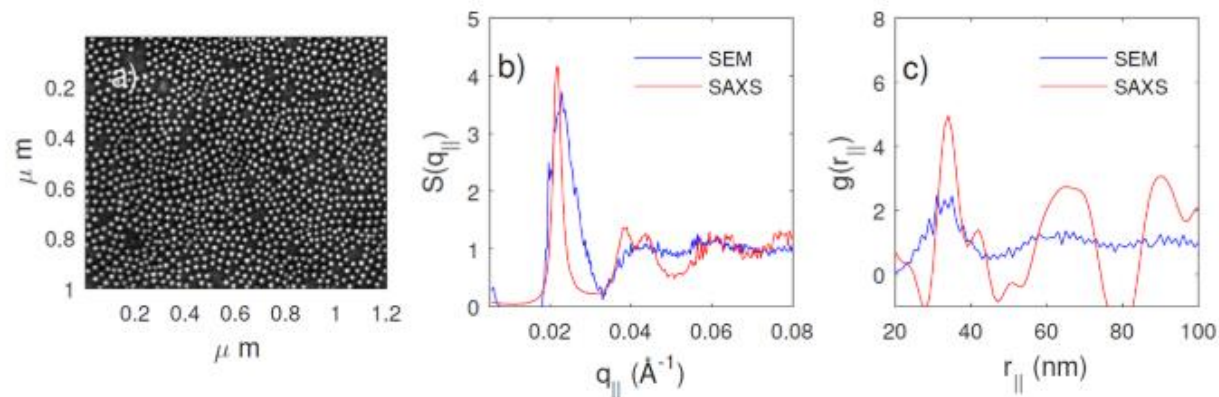
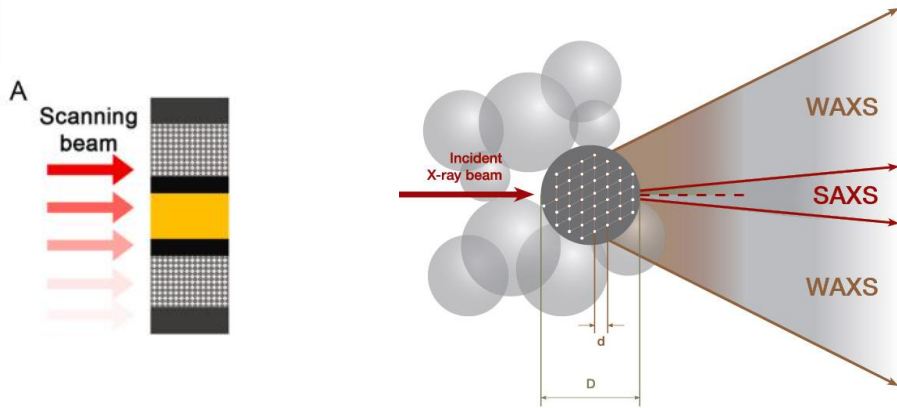


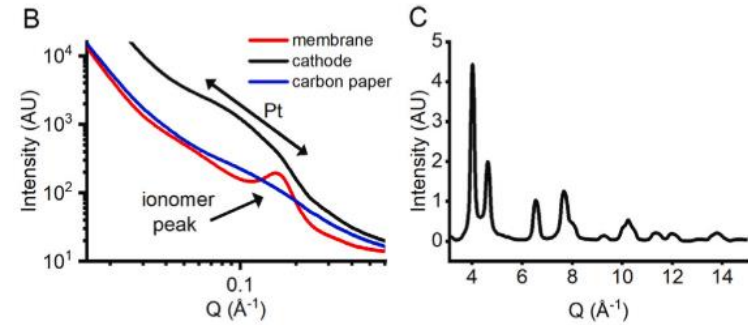
Figure 14. (a) SEM image of 15 nm DNA-conjugated gold nanoparticles (DNA–AuNPs) hybridized to DNA modified substrates. (b) Structure factors calculated from SEM and experimental SAXS data. (c) The pair distribution function calculated from the structure factor in (b) shows sharper peaks and clearer hexagonal symmetry than the pair distribution function calculated from the SEM in (a), likely because of better statistics. Reproduced from ref 129. Copyright 2014 American Chemical Society.

Chem. Rev. 2016, 116, 18, 11128–11180

X-RAY SCATTERING / CASE OF STUDY

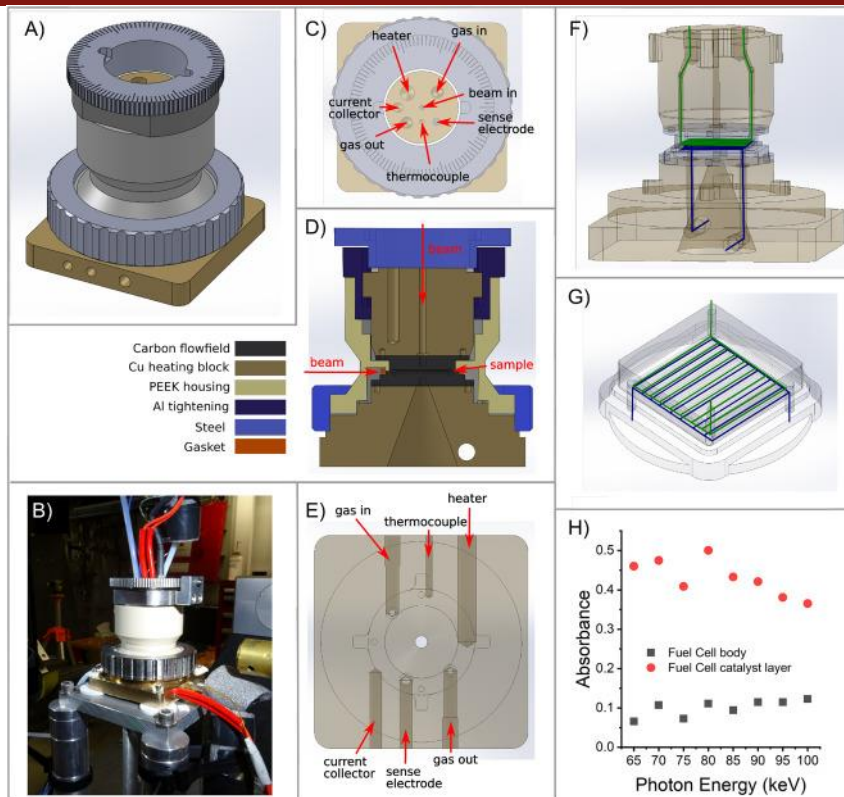


<https://wiki.anton-paar.com/cn-cn/saxs-nanostructure-analysis/>



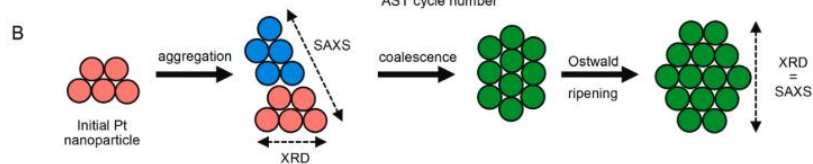
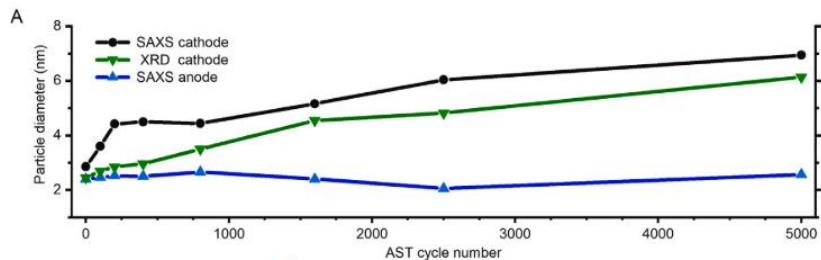
Martens, Journal of Power Sources 521 (2022) 230851

X-RAY SCATTERING / CASE OF STUDY

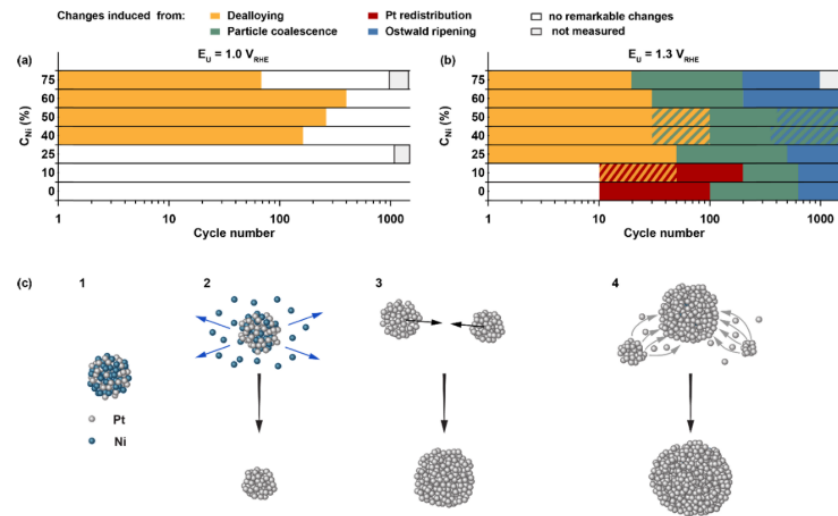


Martens, Journal of Power Sources 437 (2019) 226906

X-RAY SCATTERING / CASE OF STUDY



Martens, Journal of Power Sources 521 (2022) 230851



Bogar, ACS Catal. 2021, 11, 11360–11370



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e Architettura**