UNIVERSITÀ
DEGLI STUDI
DI TRIESTE

Dipartimento di
Ingegneria
e Architettura

FUEL CELLS AND BATTERIES
TECHNIQUES AND STANDARDS OF CHARACTERIZATION

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A.A. 2022-2023

OUTLINE

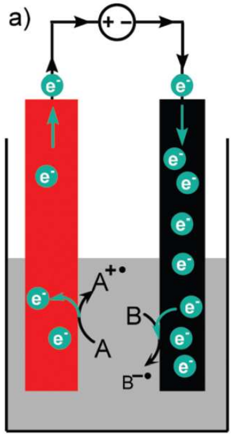
1. Dependency of fuel cell performances on input parameters
2. Dependency of batteries performances on input parameters
3. Standard for fuel cells testing
4. Standard for batteries testing
5. Investigation techniques for characterization of electrochemical systems

PART 1

1. **Dependency of fuel cell performances on input parameters –** The fuel cells an their operating principles; the main physical quantities which need to be monitored for characterizing fuel cell performances
2. Dependency of batteries performances on input parameters
3. Standard for fuel cells testing
4. Standard for batteries testing
5. Investigation techniques for characterization of electrochemical systems

ELECTROCHEMISTRY AND THE ELECTROCHEMICAL CELL

Electrochemistry is the science dealing with the interconversion of electrical and chemical energies.
In particular, it deals with chemical reactions in which an electron transfer takes place in between two conductive electrodes, divided by an insulating and ionically conductive electrolyte.



Schotten C., Green Chem., 2020,22, 3358-3375

An electrochemical cell is a general device capable of converting chemical energy into electrical one. If current is generated during cell operation, the electrochemical cell is also known as Galvanic electrochemical cell.

In example, the electrochemical cell can be viewed as the fundamental brick constituting batteries.

REDOX (REDUCTION-OXIDATION) REACTIONS

Redox, is a term used to describe a couple of specular electrochemical reactions.

$$aA + bB \rightleftharpoons cC + dD$$

Composed by:

Reduction reaction

the oxidation number of a specimen is reducing (+ e^-)

$$M^{n+} + ne^- \rightarrow M$$

Oxidation reaction

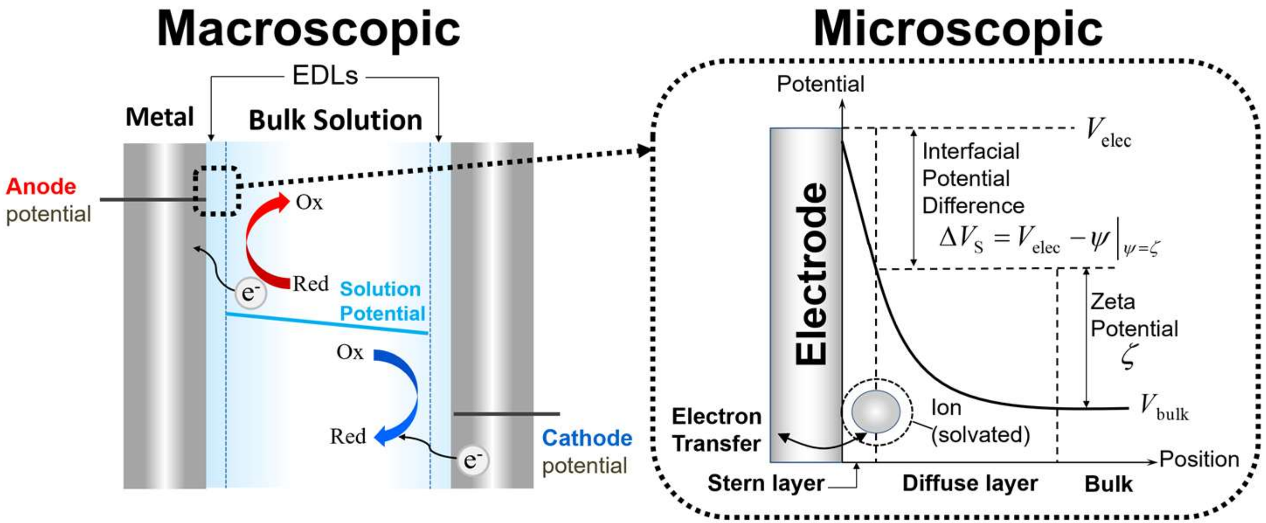
the oxidation number of a specimen is increasing (- e^-)

$$M \rightarrow M^{n+} + ne^-$$

PROCESSES AT THE ELECTRODE SURFACE

Processes involved in electrochemical reactions:

1. Transport by diffusion or migration of EC active species towards electrode surface
2. The EC active atom/ion has to adsorb a the electrode surface
3. Charge transfer (redox) has to take place
4. The reacted atom/ion has to desorb the electrode surface
5. It migrates back in the electrolyte bulk



https://nanolab.engineering.ucsb.edu/research/electrochemistry-nanoscale

FUEL CELLS – A BRIEF RECALL

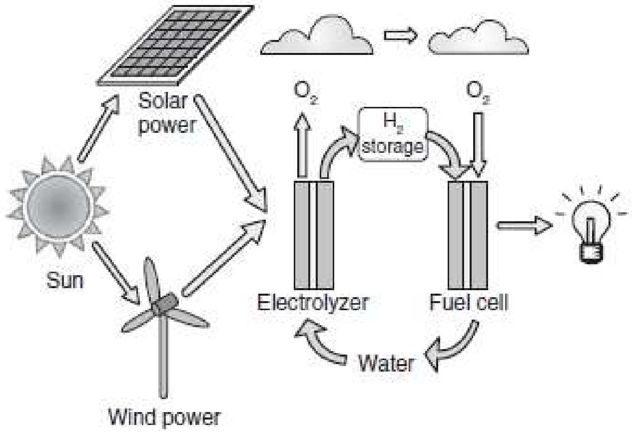
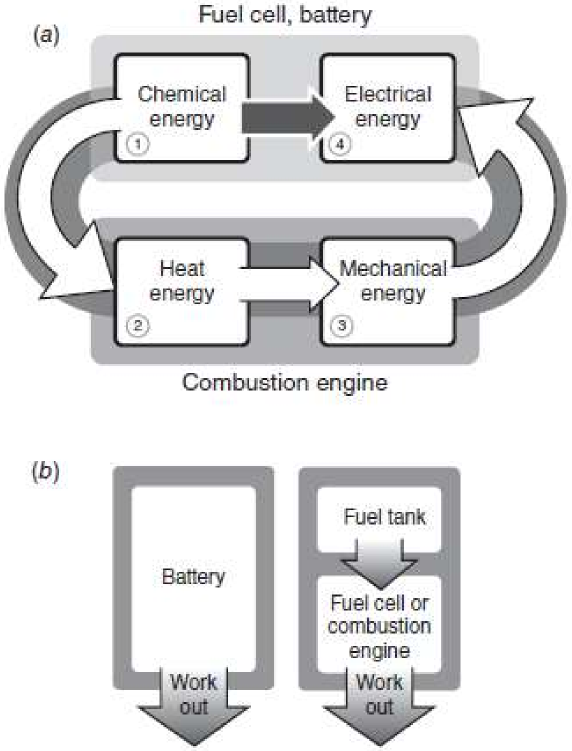


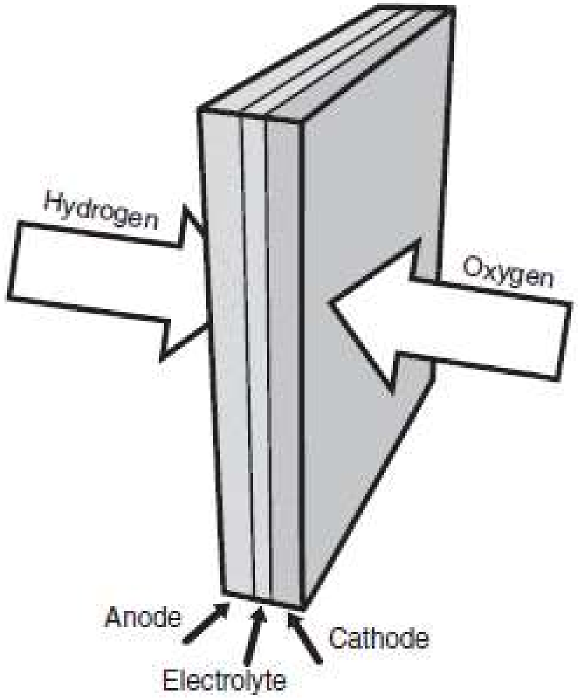
Figure 1.1. General concept of a (H_2–O_2) fuel cell.



FUEL CELLS – A BRIEF RECALL

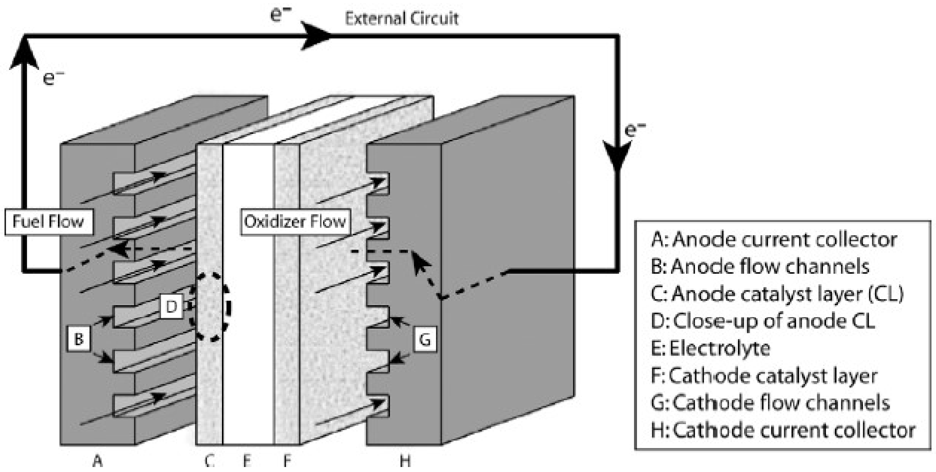
There are five major types of fuel cells, differentiated from one another by their electrolyte:

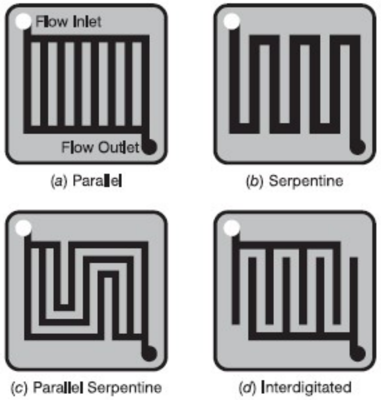
1. Phosphoric acid fuel cell (PAFC)
2. Polymer electrolyte membrane fuel cell (PEMFC)
3. Alkaline fuel cell (AFC)
4. Molten carbonate fuel cell (MCFC)
5. Solid-oxide fuel cell (SOFC)



	PEMFC	AEMFC
Anode	$H_2 \rightarrow 2H^+ + 2e^-$	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$
Cathode	$2H^+ + 2e^- + \frac{1}{2}O_2 \rightarrow H_2O$	$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$
Total	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

FUEL CELLS – A BRIEF RECALL





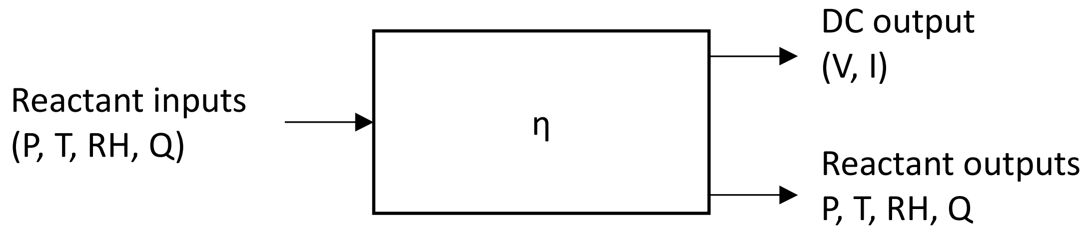
(a) Parallel

(b) Serpentine

(c) Parallel Serpentine

(d) Interdigitated

FUEL CELLS – A BRIEF RECALL



Reactant inputs
(P, T, RH, Q)

η

DC output
(V, I)

Reactant outputs
P, T, RH, Q

The yield of the process is defined by the ratio between the produced electrical energy and the chemical energy brought by the reactants.

But:

- While the electrical energy can be easily determined as: $V \cdot I \cdot t$
- The chemical energy brought by the reactants require to define a setpoint has to be defined (in terms of T and P).

For the general fuel cells:

$$\eta = \frac{V \cdot I \cdot t}{\Delta G}$$

$$\Delta G = G(products) - G(reactants)$$

FUEL CELLS – THERMODYNAMICS

The Gibbs free energy is a thermodynamic description of a system that depends on T and P (instead of S and V) and the maximum amount of work that may be performed by a thermodynamically closed system. When applied to fuel cell systems, Gibbs free energy represents the maximum chemical energy available for conversion to useful work.

The Gibbs free energy is defined as

$$G = H - TS \quad \rightarrow \quad dG = dH - SdT - TdS$$

From the definition of enthalpy ($H = U + PV$), the Gibbs free energy can be expressed as:

$$dG = dU + PdV + VdP - SdT - TdS$$

Where:

$$dU = TdS - dW = TdS - dW_m - dW_e = TdS - PdV - dW_e$$

Thus, at constant T and P:

$$dG = TdS - PdV - dW_e + PdV - VdP\Big|_{dP=0} - SdT\Big|_{dT=0} - TdS$$

$$\downarrow$$

$$\boxed{dG = -dW_e}$$

FUEL CELLS – THERMODYNAMIC EFFICIENCY

From this, two voltages can be defined:

1. The maximum expected voltage, which derives from the definition of the electromotive force:

$$\overline{w}_e = nFE \quad (J) = \left(\frac{e^-_{eq}}{mol}\right)\left(\frac{C}{e^-_{eq}}\right)\left(\frac{J}{C}\right)$$

   The maximum expected voltage without any polarization losses can be expressed as:

$$E^0 = -\frac{\Delta G}{nF}$$

   In a fuel cell it is also known standard reversible voltage

2. If all of the available chemical energy would then be converted into electrical one, and no heat transfer would take place, there would be no entropy change and the differential change of Gibbs free energy would be equal to differential enthalpy:

$$dG = dH$$

   In these (ideal) conditions, the maximum available voltage for a reversible and adiabatic system can be defined as:

$$E_{th} = -\frac{\Delta H}{nF}$$

   Which defines the theoretical maximum limit of the process

FUEL CELLS – OPEN CIRCUIT VOLTAGE

The OCV represents the maximum voltage which is characterizing a fuel cell disconnected from any load.

A generic redox reaction can be described as:

$$v_A A + v_B B \rightarrow v_C C + v_D D$$

Where v_x are the chemical stoichiometric coefficients. For a system at the equilibrium:

$$\Delta G = \Delta G^0(T) - RT \ln\left(\frac{a_A^{v_A} a_B^{v_B}}{a_C^{v_C} a_D^{v_D}}\right)$$

Where ΔG^0 is the standard free energy variation of the redox reaction and a_x are the thermodynamic activity coefficients for the involved reacting species.

FUEL CELLS – OPEN CIRCUIT VOLTAGE

But the thermodynamic activity coefficients are dependent on both the reference pressure for the system (usually atmospheric pressure, P^0) and the partial pressure of the gases fed at the fuel cell (P_x):

$$a_x = \frac{P_x}{P^0}$$

Thus, the Open Circuit Voltage of a fuel cell, is related to the standard Gibbs free energy of the reaction and to the reaction kinetics by means of the Nernst equation:

$$E(P,T) = -\frac{\Delta G^0(T)}{nF} + \frac{RT}{nF}\ln\left(\frac{(P_A/P^0)^{\nu_A}(P_B/P^0)^{\nu_B}}{(P_C/P^0)^{\nu_A}(P_D/P^0)^{\nu_B}}\right)$$

Which underlines as OCV is dependent on both the working temperature and the partial pressure of the supplied gases-

FUEL CELLS – RH

Partial pressure is then a crucial parameter to be monitored because it determines the internal relative humidity (RH) at which the redox reaction is taking place. This is strongly affecting the production of liquid water and the consequent water management issues

The gas pressure can be expressed as a sum of atmospheric partial pressure and a vapor partial one:

$$P_x = P_a + P_v$$

the RH is thus defined as:

$$RH(\%) = \frac{P_v}{P_{v,sat}}$$

Where $P_{v,sat}$ is the maximum vapor pressure at the thermodynamic equilibrium (from tabulated values; *e.g.* $P_{v,H_2O}(T)\big|_{T=100°C} = P_{atm}$).

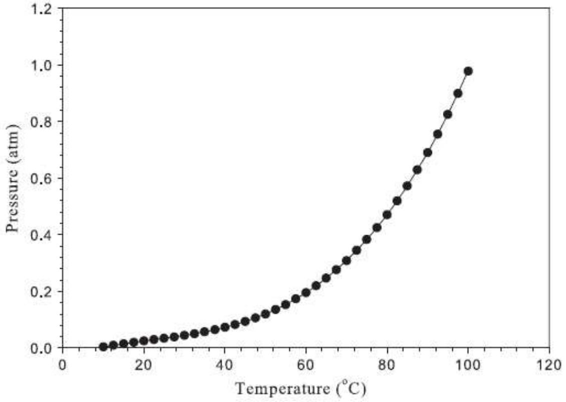


Figure 3.12 Saturation pressure versus temperature for water.

FUEL CELLS – FARADIC EFFICIENCY

Finally, in a real fuel cell not all of the amount of gases fed into a fuel cell undergo redox reactions. In order to define the efficiency of the process, the gaseous stoichiometry (at the electrode) has been defined as

$$\lambda_{C(A)} = \frac{1}{Faradic\ efficiency, \varepsilon_{C(A)}} = \frac{actual\ rate\ of\ oxidizer\ (fuel) delivered\ to\ cathode\ (anode)}{theoretical\ rate\ of\ oxidizer\ (fuel) required}$$

And is related to the Faradic efficiency, which is a measure of the percent utilization of a reactant in a galvanic process.

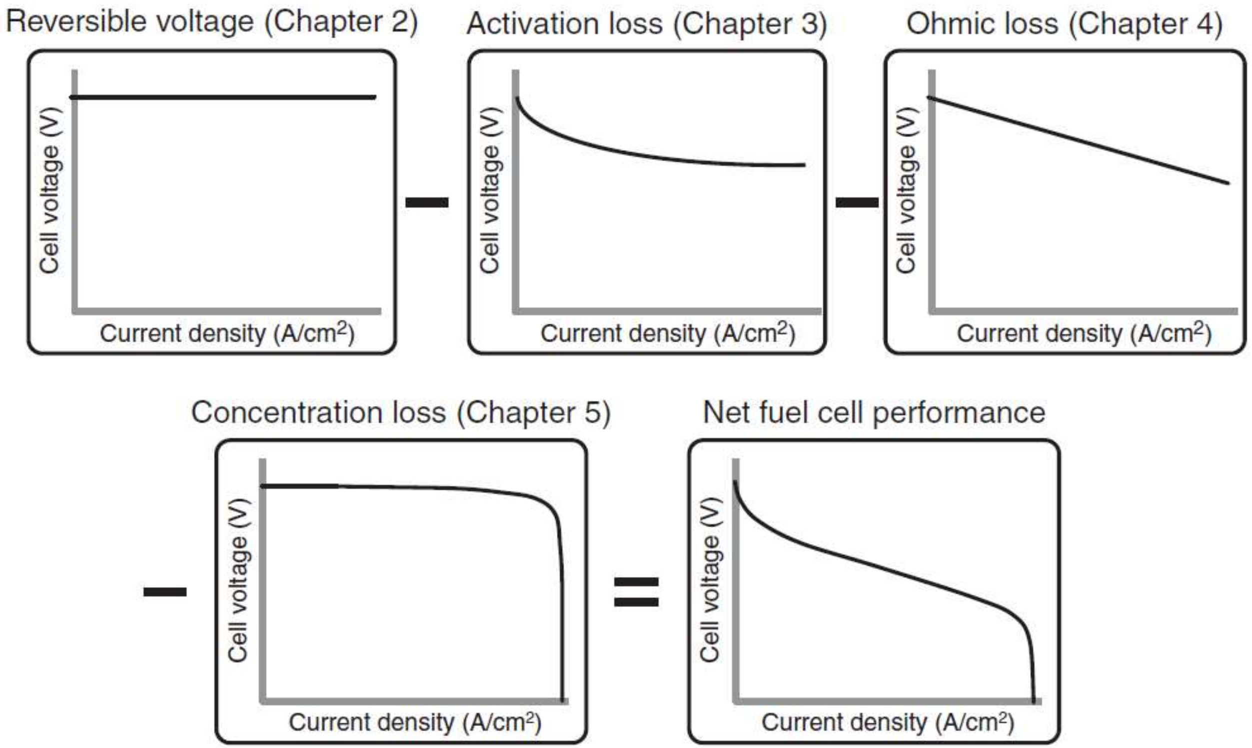
The rate of molar consumption or production of the x-specimen ($\dot{n}_x$) which is participating in current generation is then related to the produced current by the Faraday's second law:

$$\dot{n}_x = \frac{jA}{nF} = \frac{I}{nF}$$

Where n is the equivalent number of electrons per mole of reactant involved in the redox reaction and F is the Faraday constant, which describes the change carried per mole of equivalent electrons involved in the redox reaction.

FUEL CELLS – THE POLARIZATION CURVE

$$V = V_{THERMODYN} - \eta_{ACT} - \eta_{OHMIC} - \eta_{CONC}$$



$$\eta_{ACT} = a_A + b_A \ln j + a_C + b_C \ln j$$

(linearized Butler-Volmer equation)

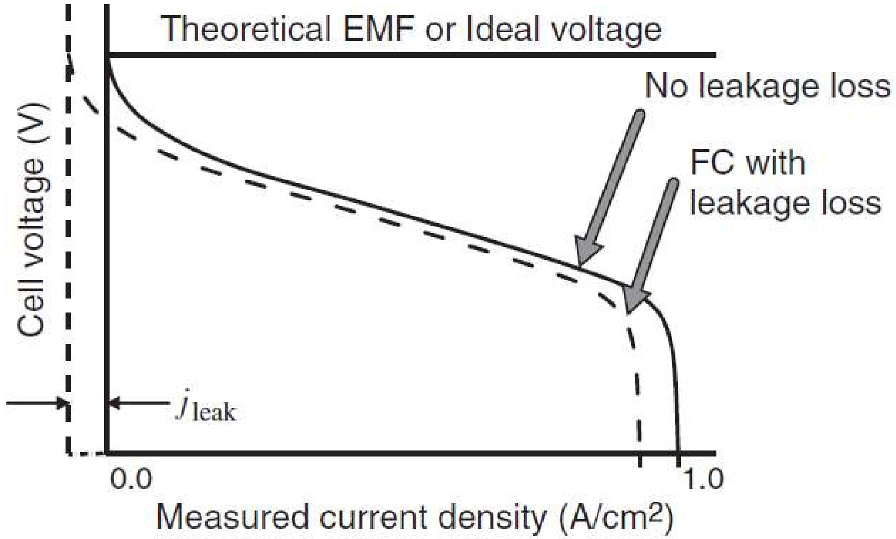
$$\eta_{OHMINC} = Rj$$

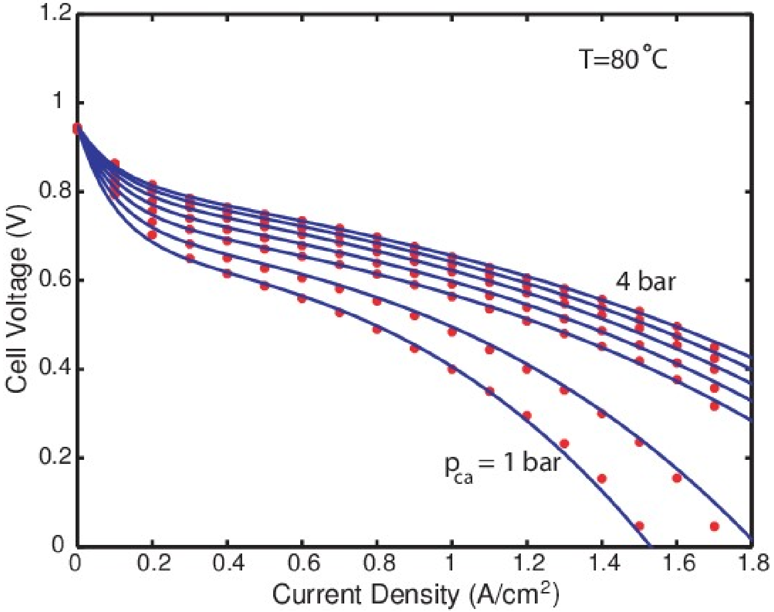
(ohm’s equation)

$$\eta_{CONC} = c \ln \frac{j_L}{j_L - j}$$

j_L limiting current density (limit case for mass transport)

FUEL CELLS – MODELLING





Pukrushpan, *Proceedings of the ASME 2002 International Mechanical Engineering Congress and Exposition*. *Dynamic Systems and Control,* 17–22, 2002. pp. 637-648.

FUEL CELLS – THE NEED OF CHARACTERIZATION

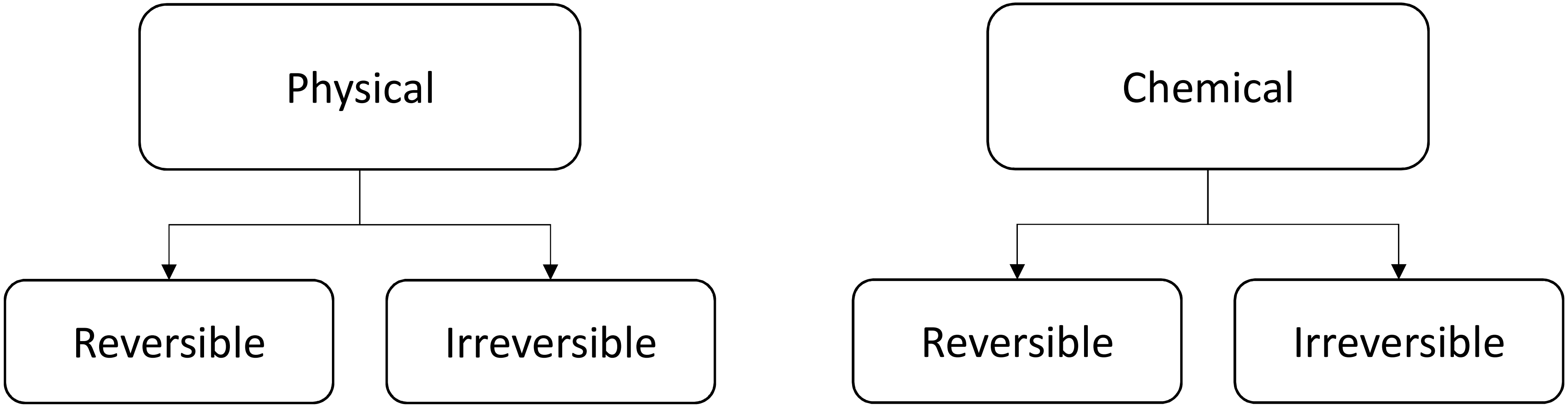
Characterization techniques allow to quantitatively compare fuel cell systems, **distinguishing good designs from poorer ones**. The most effective characterization techniques also indicate **why a fuel cell performs the way it does**.

Answering these *why* questions requires sophisticated testing techniques that can pinpoint performance bottlenecks. In other words, the best characterization techniques discriminate between the various sources of loss within a fuel cell: fuel crossover, activation, ohmic, and concentration losses.

FUEL CELLS – DEGRADATION MECHANISMS

System and electrochemical measurements are required to detect degradation mechanisms and improve cell design.

Due to the complex architecture of fuel cell systems, degradation mechanisms can be classified as:


Physical

Reversible

Irreversible

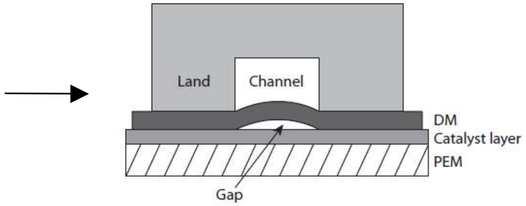
Chemical

Reversible

Irreversible

FUEL CELLS – PHYSICAL REVERSIBLE DEGRADATION MECHANISMS

Diffusion Media Channel Intrusion The result is a lack of contact with the catalyst layer under the channel and excessive pressure drop in the affected channel. In large stacks this can cause severe flow maldistribution effects and the gap created can serve as a liquid pooling location under the diffusion media.



Flooding or Dry out Due to wrong flow rate of reactants or coolant and inlet humidification or coolant flow modification.

Reactant Starvation If a location in the catalyst layer of the anode or cathode is blocked with liquid or the flow rate to a stack cell is reduced due to maldistribution, poor performance from fuel or oxidizer starvation can result. Prolonged fuel starvation may result in voltage reversal and in some cases carbon corrosion.

Voltage Reversal (Benign) Some fuel cell voltage reversal reactions are benign and thus reversible as soon as conditions in the cell are returned to normal.

Physical Intrusion of Unwanted Particulate Matter Dirt, sand, and other foreign matter it in the air can be brought into the fuel cell and block flow channels.

FUEL CELLS – PHYSICAL IRREVERSIBLE DEGRADATION MECHANISMS

Diffusion Media Plastic Deformation Due to exceeded pressure applied to the diffusion media which results drastically deformed (or damaged)

Catalyst Layer Cracking and Delamination Related to catalyst layers in which annealing is used for catalyst fixation to the substrate. Here, small fissures are common in catalyst layers. Over time, and as a result of the electrolyte expansion and contraction with water content variation, these cracks can grow and lead to delamination or catalyst layer degradation.

Electrolyte Fracture Electrolyte fracture can result from rapid or severe temperature and or humidity cycling, including frozen conditions, resulting in increased hydrogen crossover, leading to failure over time.

Diffusion Media Hydrophobicity Change The wettability of the diffusion media can change over time (due to prolonged operation or impurity presence), altering the water management and increasing flooding.

Morphology Changes or Loss in Catalyst Layer or Other Components For all fuel cells, the catalyst layer ECSA is a determining factor in overall power density, and nanosized catalysts and supports are present in a complex three-dimensional electrode structure designed to simultaneously optimize electron, ion, and mass transfer. As a result, any morphological changes can result in reduced performance. Commonly observed phenomena include catalyst sintering, dissolution and migration, catalyst oxidation, supporting material oxidation (e.g., carbon corrosion for carbon-supported catalysts), and Oswald ripening.

Pinhole Formation As a result of internal stresses, localized hot spots and dry out, small pinholes can develop in the electrolyte. This leads to a gradually increasing hydrogen crossover problem and eventual failure.

FUEL CELLS – CHEMICAL REVERSIBLE DEGRADATION MECHANISMS

Gas-Phase Impurities There are several different species that preferentially absorb on the catalyst surface and can degrade the electrochemical activity of that surface (among the others: dust, hydrocarbons, ammonia, sulphur-containing gases, …). Platinum oxides on the surface of a catalyst can be cleansed with a quick excursion to low cell voltages (<0.4 V). Among these, Carbon monoxide (CO) poisoning is due to the small amounts of CO present on hydrogen produced by hydrocarbon reforming.

Coolant Conductivity Increase Since the coolant system is in contact with the entire stack, the coolant must be highly nonconductive. Over time, ionic impurities in the coolant stream can degrade the coolant performance, causing shorting within the stack and reducing performance.

FUEL CELLS – CHEMICAL IRREVERSIBLE DEGRADATION MECHANISMS

Electrolyte Loss For PEMFCs, the electrolyte can degrade physically (mechanical stress) and chemically (peroxide radical attack). This results in loss of mass and conductivity in the electrolyte and possibly pinhole formation. Electrolyte thinning This can results in a temporary increase in performance (reduced ohmic losses). However, over time, the electrolyte is more susceptible to pinhole formation and excessive crossover, leading to failure.

Platinum Dissolution and Migration Due to unwanted reactions at the cathode, it result is an irreversible loss of catalyst with fewer active sites in the cathode (ECSA reduction) and in a decrease of exchanged current density cathode.

Ionic Impurity Contamination Ionic metal impurities from metals can readily absorb into the fuel cell electrolyte and it can greatly reduce the ionic conductivity and alter water transport.

FUEL CELLS – THE OBJECTS OF CHARACTERIZATION

- Overall performance (j/V curve, power density)
- Kinetic properties (η_{act}, j_0, α, Electrochemically Active Surface Area ECSA)
- Ohmic properties (R_{ohmic}, electrolyte conductivity, contact resistances, electrode resistances, interconnection resistances)
- Mass transport properties (j_L, D_{eff}, pressure losses, reactant/product homogeneity)
- Parasitic losses (j_{leak}, side reactions, fuel crossover)
- Electrode structure (porosity, tortuosity, conductivity)
- Catalyst structure (thickness, porosity, catalyst loading, particle size, ECSA, catalyst utilization, triple phase boundaries, ionic conductivity, electrical conductivity)
- Flow structure (pressure drop, gas distribution, conductivity)
- Heat generation/heat balance
- Lifetime issues (lifetime testing, degradation, cycling, start-up/shut-down, failure, corrosion, fatigue)

FUEL CELLS – THE OBJECTS OF CHARACTERIZATION

- Overall performance (j/V curve, power density)

The best fuel cell under test is the one which is able to deliver the highest voltage at the current density of interest.

Of course, fuel cell j/V performance can change dramatically depending on factors like the operating conditions and testing procedures. To ensure that j/V performance comparisons are fair, identical operating conditions, testing procedures and device history must be provided.

FUEL CELLS – THE OBJECTS OF CHARACTERIZATION

- Kinetic properties (η_{act}, j_0, α, Electrochemically Active Surface Area ECSA)
- Ohmic properties (R_{ohmic}, electrolyte conductivity, contact resistances, electrode resistances, interconnection resistances)
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- Lifetime issues (lifetime testing, degradation, cycling, start-up/shut-down, failure, corrosion, fatigue)

All of these phenomena concur in determining the fuel cell behaviour

FUEL CELLS – THE OBJECTS OF CHARACTERIZATION

As a consequence, it is considerably more difficult to understand why a given fuel cell performs the way it does.

Generally, the best way to tackle this problem is to think about a fuel cell's performance in terms of the various major loss categories: activation loss, ohmic loss, concentration loss, and leakage loss.

If we can somehow determine the relative sizes of each of these losses, then we are closer to understanding our fuel cell's problems.

FUEL CELLS – TESTING CONDITIONS

Test and operative conditions are needed to be accurately recorded because dramatically affect fuel cell performance. For example, a “bad” PEMFC operating at 80°C on humidified oxygen and hydrogen gases under 5 bar pressure may show better *j*/*V* curve performance than a “good” PEMFC operating at 30°C on dry air and dilute hydrogen at atmospheric pressure. Only if the two fuel cells are tested under identical conditions, the truly good fuel cell will become apparent.

$$E(P,T) = -\frac{\Delta G^0(T)}{nF} + \frac{RT}{nF}\ln\left(\frac{(P_A/P^0)^{v_A}(P_B/P^0)^{v_B}}{(P_C/P^0)^{v_A}(P_D/P^0)^{v_B}}\right)$$

FUEL CELLS – TESTING CONDITIONS

Warm-up

To ensure that a fuel cell system is well equilibrated, it is customary to conduct a standardized warm-up procedure prior to cell characterization. A typical warm-up procedure might involve operating the cell at a fixed current load for 30 ÷ 60 minutes prior to testing. Failure to properly warm up a fuel cell system can result in highly nonstationary (non-steady-state) behaviour.

FUEL CELLS – TESTING CONDITIONS

Temperature

It is important to document and maintain a constant fuel cell temperature during measurement. Both the gas inlet and exit temperatures should be measured as well as the temperature of the fuel cell itself. Sophisticated techniques even allow temperature distributions across a fuel cell device to be monitored in real time. In general, increased temperature will improve performance due to improved kinetics and conduction processes (For PEMFCs, this is only true up to about 80°C, above which membrane drying becomes an issue).

FUEL CELLS – TESTING CONDITIONS

Flow Rate

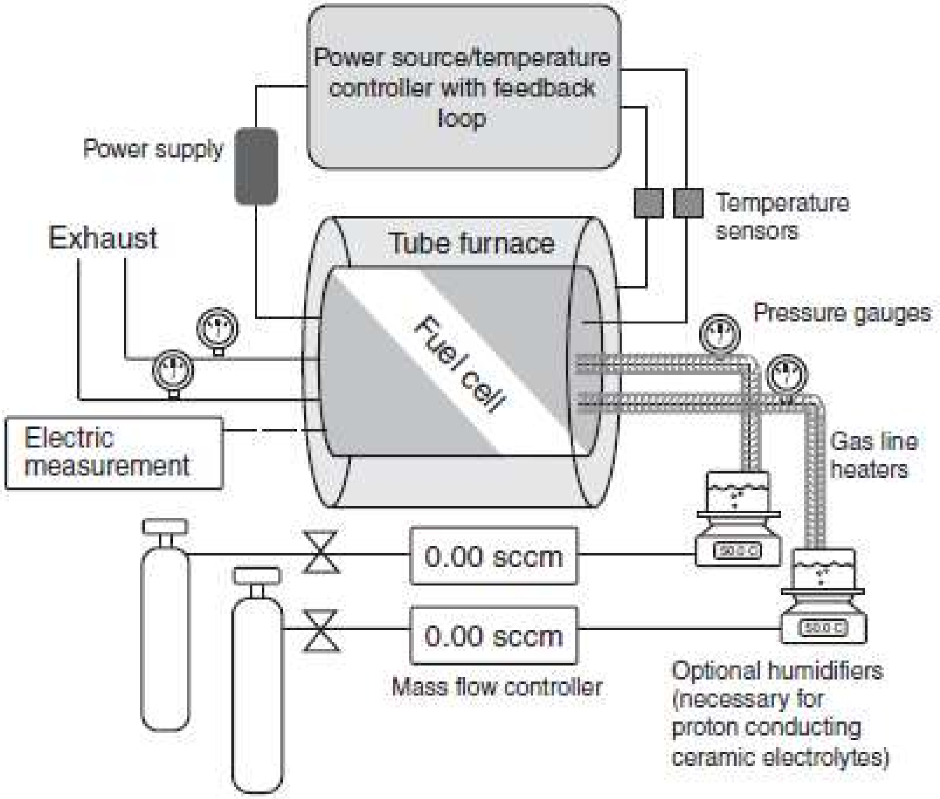
Flow rates are generally set using mass flow controllers. During a j/V test, there are two main ways to handle reactant flow rates. In the first method, flow rates are held constant during the entire test at a flow rate that is sufficiently high so that even at the largest current densities there is sufficient supply. This method is known as the fixed-flow-rate condition. In the second method, flow rates are adjusted stoichiometrically with the current so that the ratio between reactant supply and current consumption is always fixed. This method is known as the fixed-stoichiometry condition. Fair j/V curve comparisons should be done using the same flow rate method. Increased flow usually improves performance (For PEMFCs, increasing the flow rate of extremely humid or extremely dry gases can upset the water balance in the fuel cell and actually decrease performance).

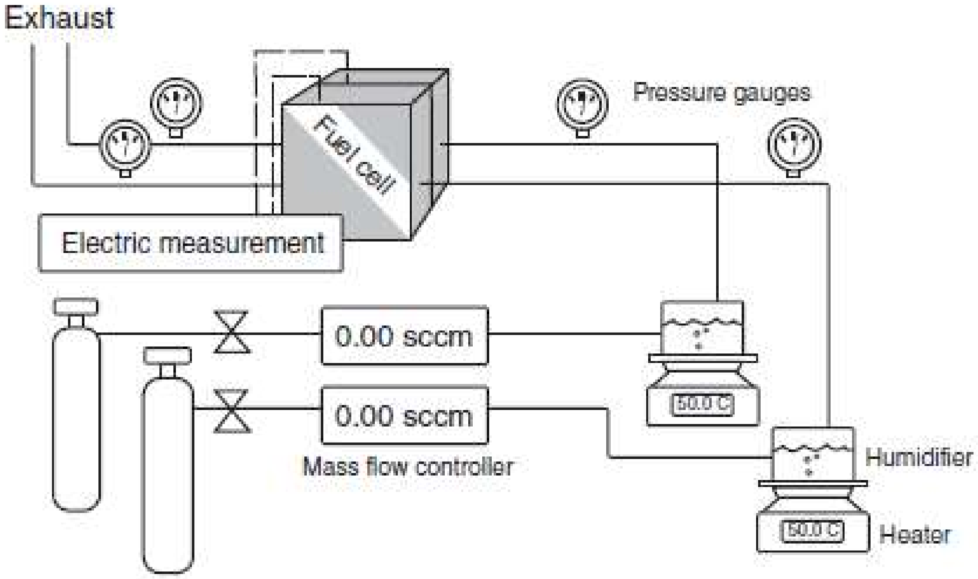
FUEL CELLS – TESTING CONDITIONS

Compression Force

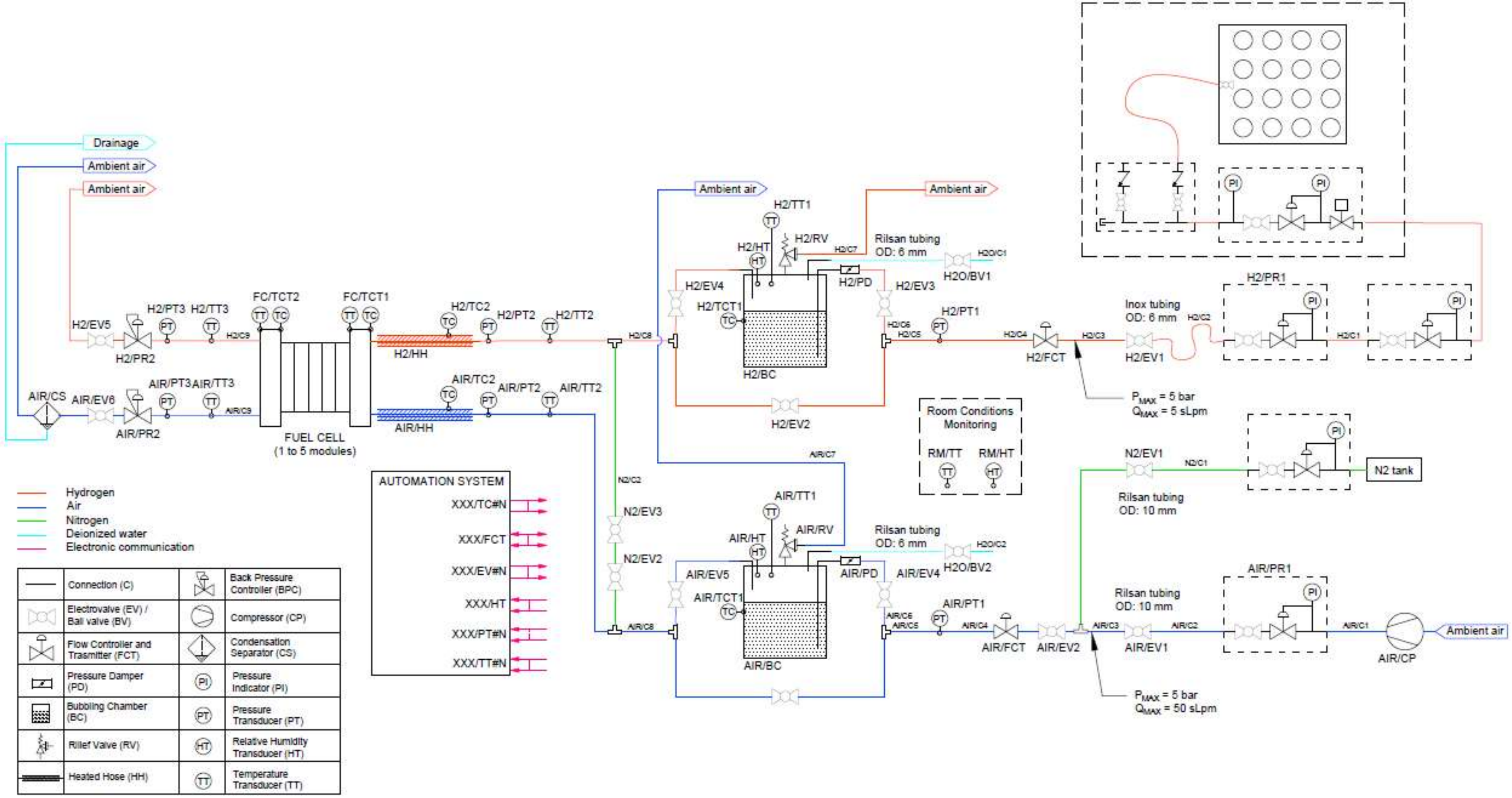
For most fuel cell assemblies, there is an optimal cell compression force, which leads to best performance; thus, cell compression force should be noted and monitored. Cells with lower compression forces can suffer increased ohmic loss, while cells with higher compression forces can suffer increased pressure or concentration losses.

FUEL CELLS – TESTING BENCHES

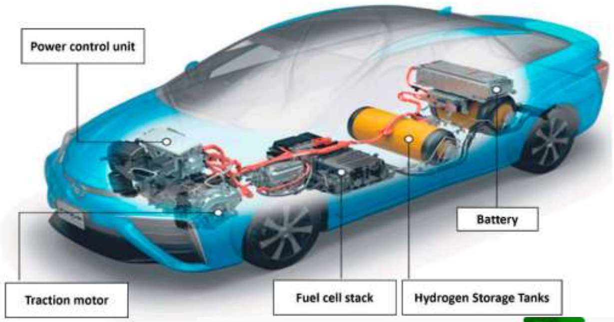


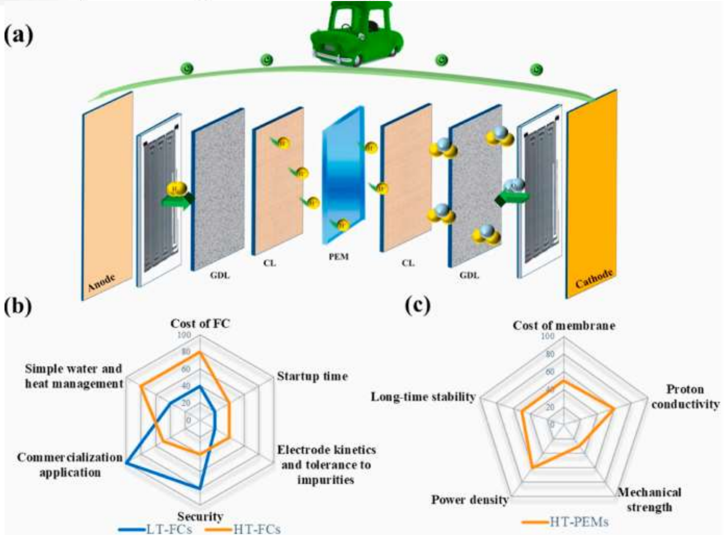


FUEL CELLS – EXAMPLE OF TEST RIG



FUEL CELLS – PERSPECTIVES





Agyekum, Membranes 2022, 12, 1103

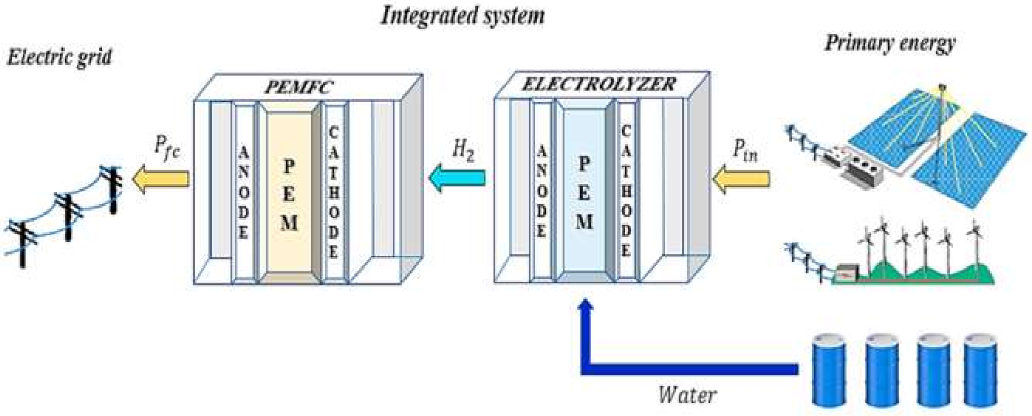


Figure 10. Diagram for Integrated Electrolyzer-fuel cell model.

R. Escobar-Yonoff, Heliyon 7 (2021) e06506

PART 2

1. Dependency of fuel cell performances on input parameters
2. **Dependency of batteries performances on input parameters** – Batteries and their operating principles; the main physical quantities which need to be monitored for characterizing batteries performances
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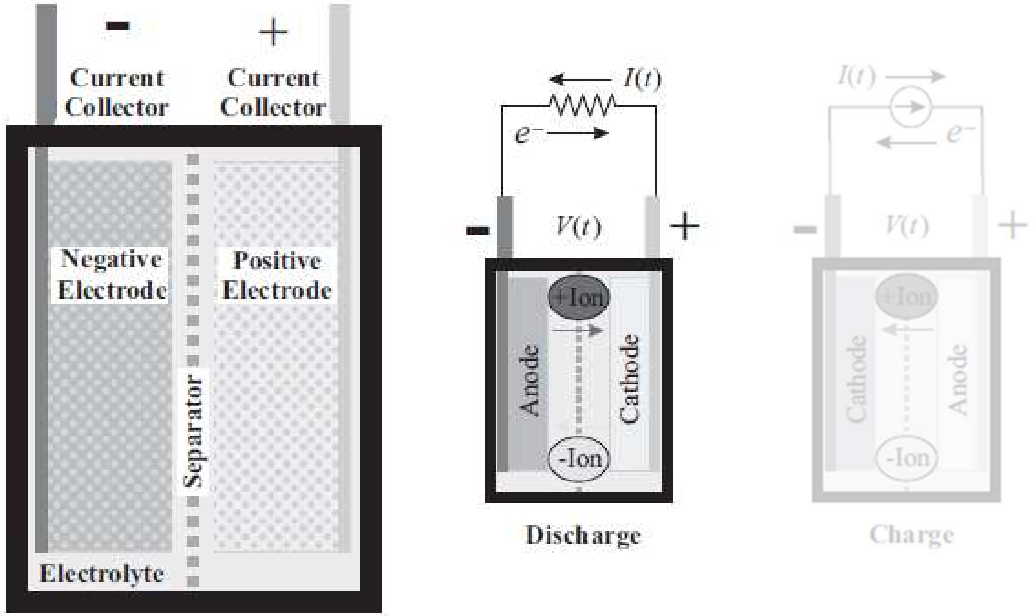
BATTERIES – A BRIEF RECALL



Discharge

Charge

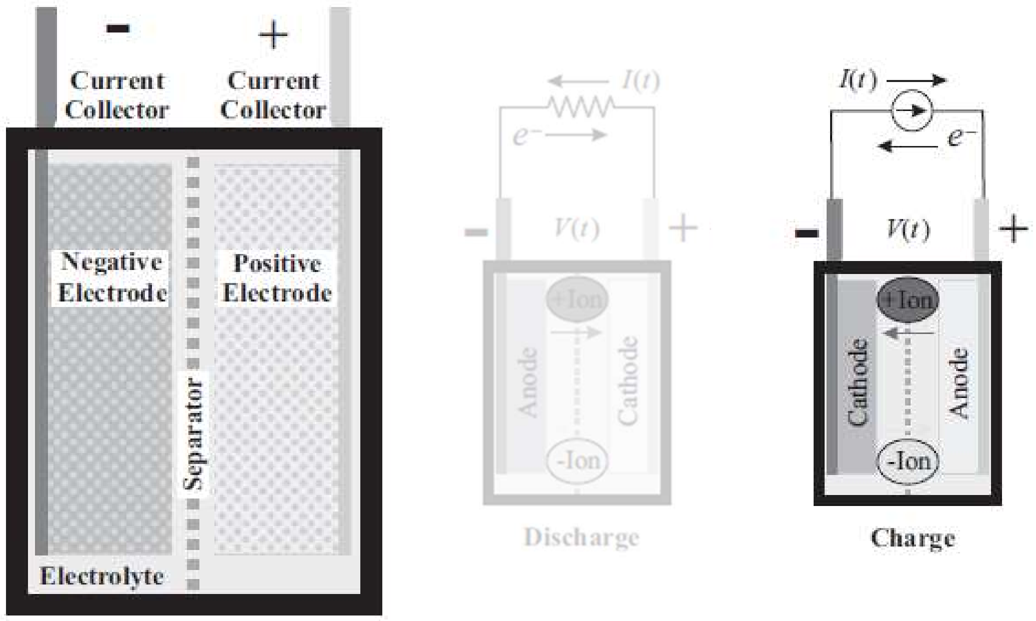
Discharge

The anode is the negative electrode, while the cathode is the positive one.

Oxidised positive ions (from oxidation reaction) move towards the cathode through the electrolyte. Negatively charged electrons flow through an external load from the anode to the cathode, creating a current in the opposite direction.

The cathode then is fed by electrons and reduction reaction hosts the positive ions within the cathode structure.

BATTERIES – A BRIEF RECALL



Charge

Now the anode is the positive electrode, while the cathode is the negative one.

At the positive electrode oxidation takes place: a positive ion is dissolved in the electrolyte solution and an electron is freed and conveyed outside of the cell.

The negative electrode is fed by electrons and the positive ions migrating across the electrolyte under the applied difference of potential. Once at the electrode, ions are reduced at the electrode surface.

BATTERIES – A BRIEF RECALL

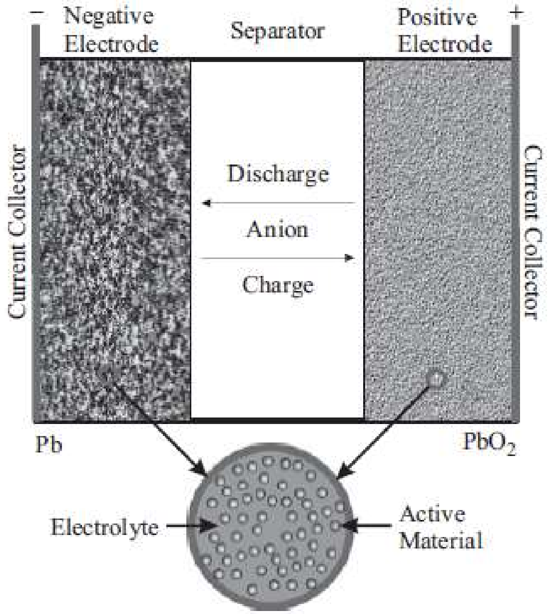


Figure 2.2 Schematic diagram of a Pb–acid cell

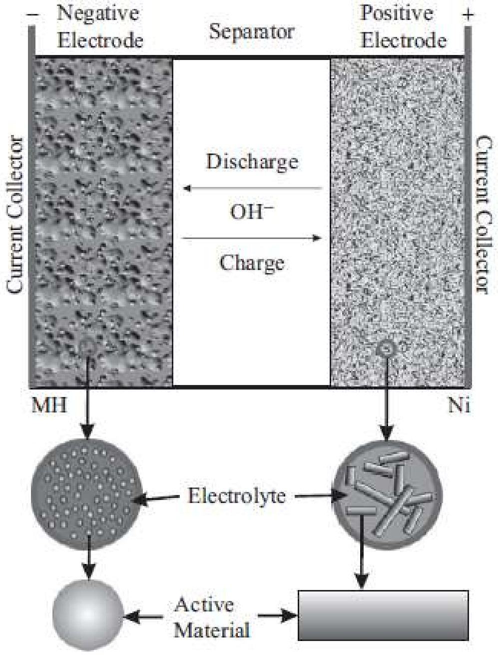


Figure 2.3 Schematic diagram of a Ni–MH cell

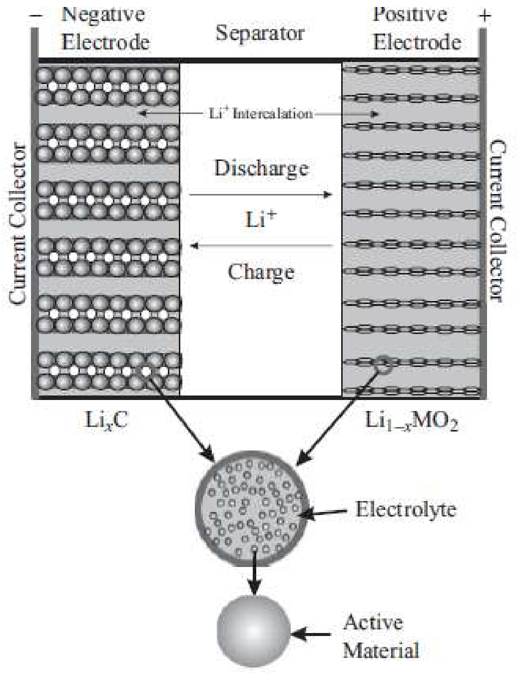


Figure 2.4 Schematic diagram of a Li-ion cell

Positive electrode: $PbO_2 + HSO_4^- + 3H^+ + 2e^- \underset{charge}{\overset{discharge}{\rightleftarrows}} PbSO_4 + 2H_2O$

Negative electrode: $Pb + HSO_4^- \underset{charge}{\overset{discharge}{\rightleftarrows}} PbSO_4 + H^+ + e^-$

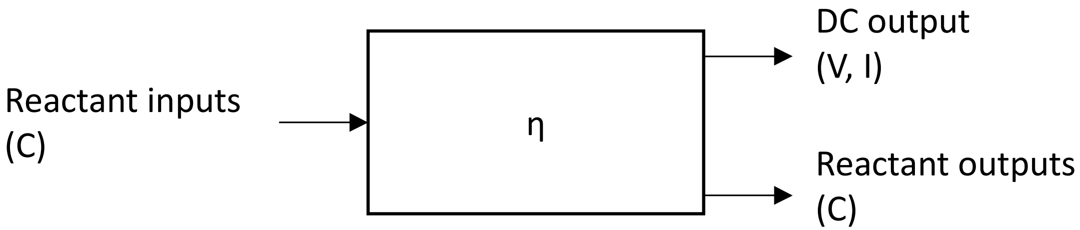
Positive electrode: $NiOOH + H_2O + e^- \underset{charge}{\overset{discharge}{\rightleftarrows}} Ni(OH)_2 + OH^-$

Negative electrode: $MH + OH^- \underset{charge}{\overset{discharge}{\rightleftarrows}} M + H_2O + e^-$

Positive electrode: $Li_{1-x}CoO_2 + xLi^+ + xe^- \underset{charge}{\overset{discharge}{\rightleftarrows}} LiCoO_2$

Negative electrode: $Li_xC \underset{charge}{\overset{discharge}{\rightleftarrows}} C + xLi^+ + xe^-$

BATTERIES – A BRIEF RECALL



The yield of the process is defined by the ratio between the charge (or the energy) stored during the charge and the charge (or the energy) drawn from the battery during its discharge. The coulombic efficiency is thus defined as:

$$\eta_C = \frac{\int_{discharge} I dt}{\int_{charge} I dt}$$

While the energy efficiency is defined as:

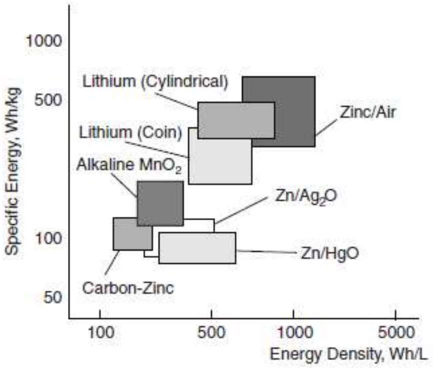
$$\eta = \frac{\int_{discharge} IV dt}{\int_{charge} IV dt}$$

BATTERIES – SPECIFIC ENERGY AND ENERGY DENSITY

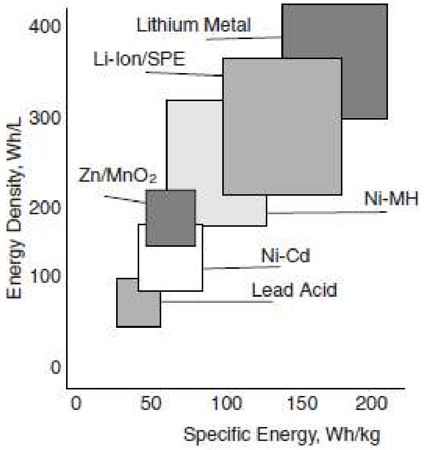
The maximum energy that can be delivered by an electrochemical system is based on the types and the amount of active materials that are used. Material type defines the battery voltage, material amounts, its capacity (Ah). Though, a divergence from the theoretical limit is always present and due to: the presence of the electrolyte (which adds mass and volume at the device) and to a reduced operative range (the battery does not charge at the theoretical voltage, nor is it discharged completely to zero). The specific energy and the energy density are two parameters which are commonly used for characterization and comparison of different battery system under different conditions of use.

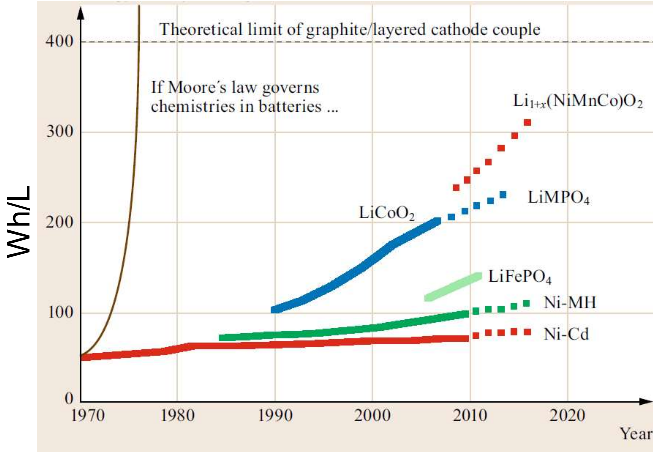
The **specific energy** expresses the energy within the battery in function of the mass of the catalyst/battery system (Wh/kg), while the **energy density** expresses the energy with respect the volume (Wh/L)

For primary batteries



For rechargeable batteries





BATTERIES – THERMODYNAMICS AND STANDARD CELL POTENTIAL

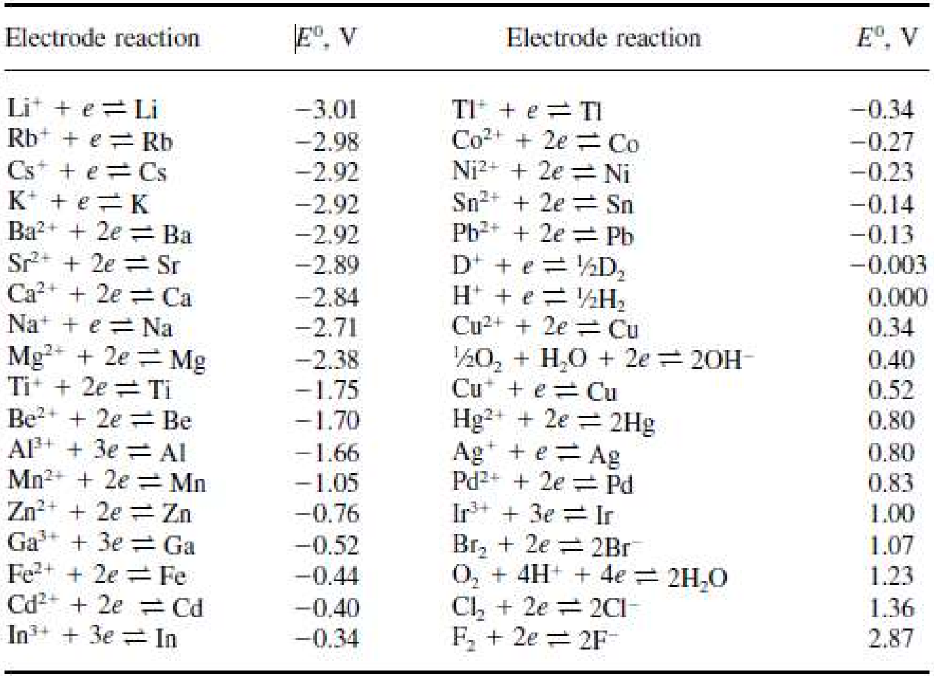
Also from batteries the Gibbs free represents represents the useful work that can be done by the cell. By means of the Gibbs-Helmholtz equation:

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

Both enthalpy and entropy of reaction depend on electrodes composition can be calculated and they can be found tabulated at standard temperature and pressure (25°C, 1 bar).

From the Gibbs free energy it is possible to retrieve the standard cell potential:

$$E^0 = -\frac{\Delta G}{nF}$$



Electrode reaction	E^0, V	Electrode reaction	E^0, V
$Li^+ + e \rightleftharpoons Li$	−3.01	$Tl^+ + e \rightleftharpoons Tl$	−0.34
$Rb^+ + e \rightleftharpoons Rb$	−2.98	$Co^{2+} + 2e \rightleftharpoons Co$	−0.27
$Cs^+ + e \rightleftharpoons Cs$	−2.92	$Ni^{2+} + 2e \rightleftharpoons Ni$	−0.23
$K^+ + e \rightleftharpoons K$	−2.92	$Sn^{2+} + 2e \rightleftharpoons Sn$	−0.14
$Ba^{2+} + 2e \rightleftharpoons Ba$	−2.92	$Pb^{2+} + 2e \rightleftharpoons Pb$	−0.13
$Sr^{2+} + 2e \rightleftharpoons Sr$	−2.89	$D^+ + e \rightleftharpoons \frac{1}{2}D_2$	−0.003
$Ca^{2+} + 2e \rightleftharpoons Ca$	−2.84	$H^+ + e \rightleftharpoons \frac{1}{2}H_2$	0.000
$Na^+ + e \rightleftharpoons Na$	−2.71	$Cu^{2+} + 2e \rightleftharpoons Cu$	0.34
$Mg^{2+} + 2e \rightleftharpoons Mg$	−2.38	$\frac{1}{2}O_2 + H_2O + 2e \rightleftharpoons 2OH^-$	0.40
$Ti^+ + 2e \rightleftharpoons Ti$	−1.75	$Cu^+ + e \rightleftharpoons Cu$	0.52
$Be^{2+} + 2e \rightleftharpoons Be$	−1.70	$Hg^{2+} + 2e \rightleftharpoons 2Hg$	0.80
$Al^{3+} + 3e \rightleftharpoons Al$	−1.66	$Ag^+ + e \rightleftharpoons Ag$	0.80
$Mn^{2+} + 2e \rightleftharpoons Mn$	−1.05	$Pd^{2+} + 2e \rightleftharpoons Pd$	0.83
$Zn^{2+} + 2e \rightleftharpoons Zn$	−0.76	$Ir^{3+} + 3e \rightleftharpoons Ir$	1.00
$Ga^{3+} + 3e \rightleftharpoons Ga$	−0.52	$Br_2 + 2e \rightleftharpoons 2Br^-$	1.07
$Fe^{2+} + 2e \rightleftharpoons Fe$	−0.44	$O_2 + 4H^+ + 4e \rightleftharpoons 2H_2O$	1.23
$Cd^{2+} + 2e \rightleftharpoons Cd$	−0.40	$Cl_2 + 2e \rightleftharpoons 2Cl^-$	1.36
$In^{3+} + 3e \rightleftharpoons In$	−0.34	$F_2 + 2e \rightleftharpoons 2F^-$	2.87

BATTERIES – THE OPEN CIRCUIT VOLTAGE

Starting from the standard cell potential it is then possible to formulate the expression from the Open Circuit Voltage (OCV). By taking into account the generic redox reaction:

$$aA + bB \rightleftharpoons cC + dD$$

the intrinsic voltage which is formed at the equilibrium is defined by the Nernst equation:

$$E = E^0 - \frac{RT}{nF} \ln\left(\frac{a_C^c a_D^d}{a_A^a a_B^b}\right)$$

where a_X are the activities of the specimens involved and E^0 is the standard electromotive force/potential for the reaction, related to the Gibbs free energy, and reaction/element-specific.

BATTERIES – OVERPOTENTIAL

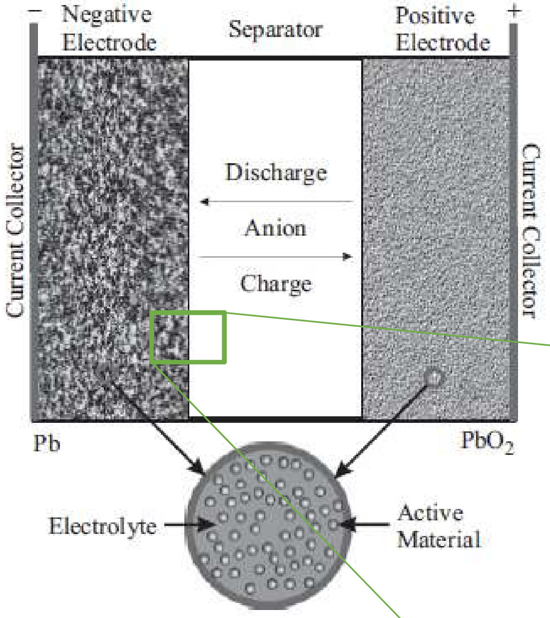
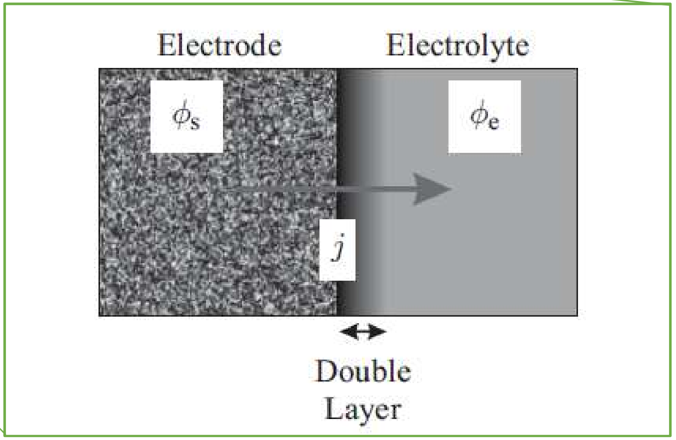


Figure 2.2 Schematic diagram of a Pb–acid cell

Batteries have porous, solid-phase electrodes that are saturated with liquid-/gel-phase electrolyte that transports ions from one electrode to the other. The electrons involved in the electrode reactions must pass through the electrode–electrolyte interface. This interface resists the flow of electrons, creating an overpotential (η) that must be overcome to allow charge transfer.



$$\eta = R_{ch.tr}\, j$$

For anodic or oxidation reactions, current flows from the electrode to the electrolyte and η > 0. For cathodic or reduction reactions, current flows from the electrolyte to the electrode and η < 0.

BATTERIES – ELECTRODE KINETICS

Electrode kinetics are described by means of the Butler-Volmer equation:

$$j = j_0\left[e^{\eta\alpha_a F/RT} - e^{\eta\alpha_c F/RT}\right]$$

Here j_0 is the exchange current density, and α_x are the anodic and cathodic exchange coefficients.

The exchange current density is a measure of the rate of exchange of charge between oxidized and reduced species at any equilibrium potential without net overall change. At equilibrium, its value equals the value of both the redox-induced anodic and the cathodic currents ($i_0 = i_a = i_c$). It defines a background for the net current which is recorded during battery operation and it depends on the concentrations of the reactants and products, on temperature, and on the nature of the solid-electrolyte interface:

$$j_0 = \frac{i_0}{A} = nFkC_0^{(1-\alpha)}C_R^{\alpha}$$

Where k is the rate of the redox reaction, C_x defines the concentration at the electrode surface and α is a parameter related to the potential energy of reaction.

The exchange coefficients are related to the number of electrons involved in the redox reactions (n):

$$\alpha_a + \alpha_c = n$$

And they are usually equal to n/2

BATTERIES – DOUBLE-LAYER CAPACITANCE

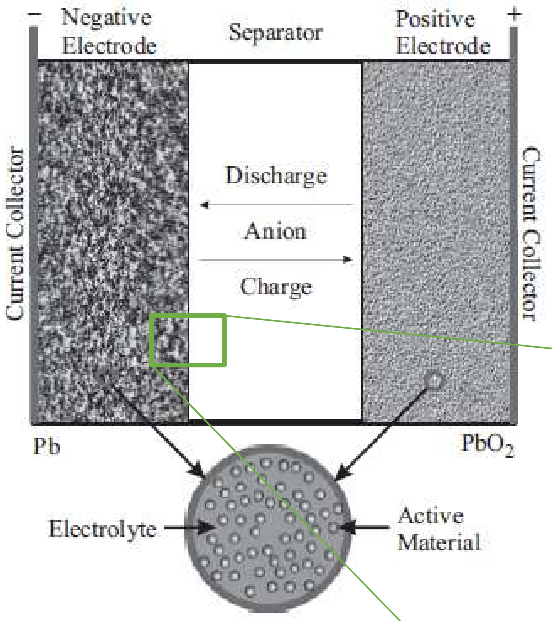
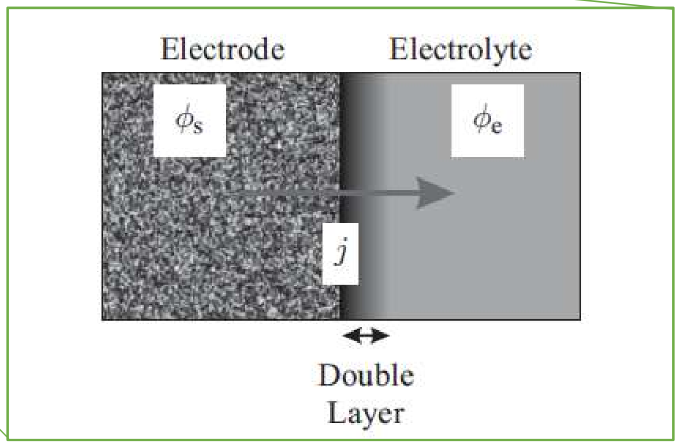


Figure 2.2 Schematic diagram of a Pb–acid cell



At the electrode-electrolyte interface the double layer is hosting specimens prone to be reduced or oxidized.

This charge accumulation induces the formation of a capacitance, called as Double Layer Capacitance:

$$i_{dl} = C_{dl}\frac{\partial \eta}{\partial t}$$

Which has to be taken into account in modelling battery systems.

BATTERIES – THE POLARIZATION CURVE

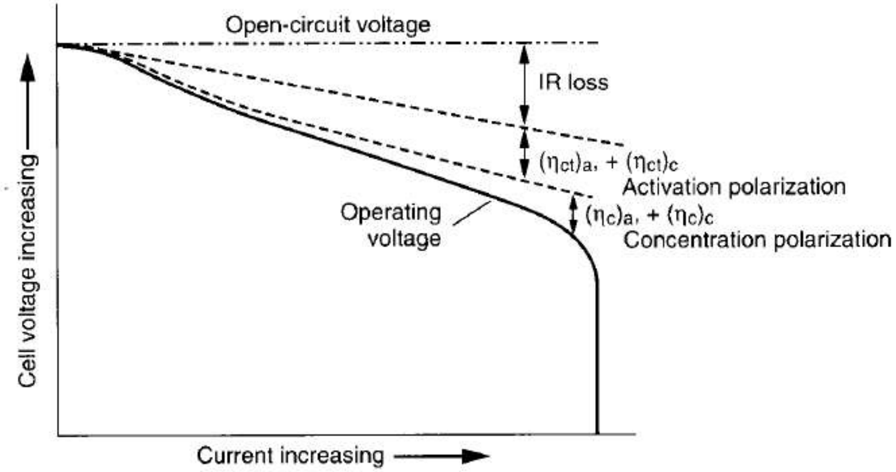


FIGURE 2.1 Cell polarization as a function of operating current.

By considering the whole battery system, there are several phenomena which are concurring in defining battery voltage:

$$V = V_{OCV} - [(\eta_{ct})_a + (\eta_c)_a] - [(\eta_{ct}) + (\eta_c)_c] - iR_i = iR$$

Where :

V_{OCV} is the open circuit voltage

(η_{ct}) describe the so called activation polarization losses due to the formation of the overpotential at the electrode-electrolyte interface

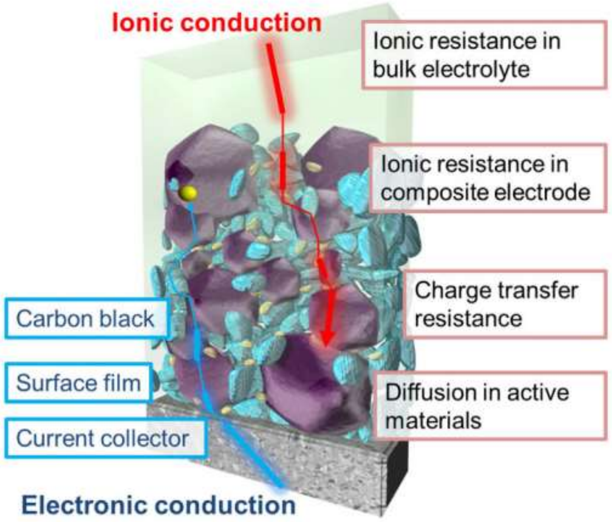
$(\eta_c)_x$ describe the so called concentration polarization losses due to the formation of the overpotential arising form the concentration of the reactants and products

iR_i are the ohmic losses due to the product of the current drawn from the battery and the battery internal resistance

BATTERIES – BATTERY INTERNAL RESISTANCE

$$R_i = \sum R_e + \sum R_i$$

$$\sum R_x = R^x_{electrolyte} + R^x_{electrodes} + R^x_{c.t.,cat/sup}$$



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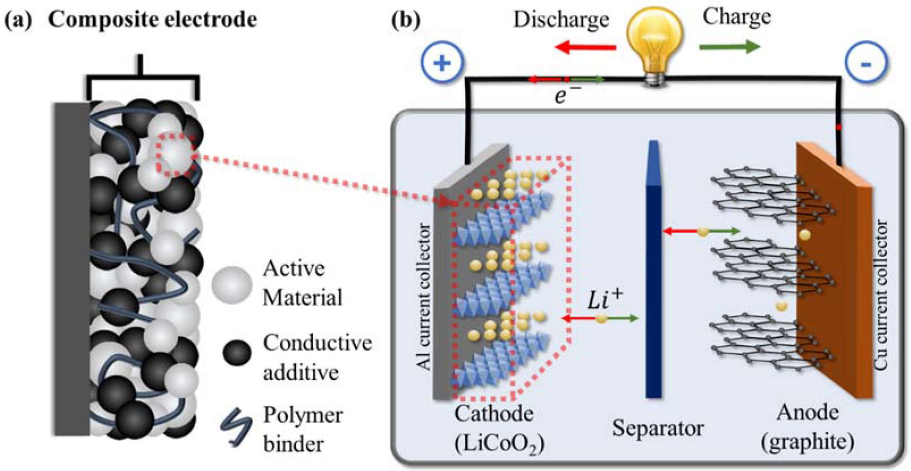


Cholewinski, *Polymers* 2021, *13*(4), 631; https://doi.org/10.3390/polym13040631

BATTERIES – MASS TRANSPORT TO THE ELECTRODE SURFACE

The main dominant phenomenon ruling mass transport to or from an electrode turns is ion diffusion in a concentration gradient and it can be described by means of the Fick's law, which defines that the flux of material crossing a plane at distance x and time t is proportional to the concentration gradient:

$$q = D_i \frac{\delta C_i}{\delta x}$$

Where D_i is the diffusion coefficient of the specimen with concentration C_i. Thus, the change of concentration over time can be expressed as:

$$\boxed{\frac{\delta C_i}{\delta t} = D_i \frac{\delta^2 C_i}{\delta^2 x}}$$

Boundary conditions selected according to the selected technique of analysis for an analytical description of the system.

In addition to diffusion also migration and convection are minor phenomena which can be used for describing transport phenomena due to the formation of enhanced electric fields in proximity of the reaction sites or to model the flow of reactants to reaction sites, respectively.

BATTERIES – CONCENTRATION POLARIZATION

The optimization of mass-transport processes is of interest in reducing the concentration polarization losses. Remembering that ion flow and produced current density can be related by means of the amount of charge exchanged during the redox reaction:

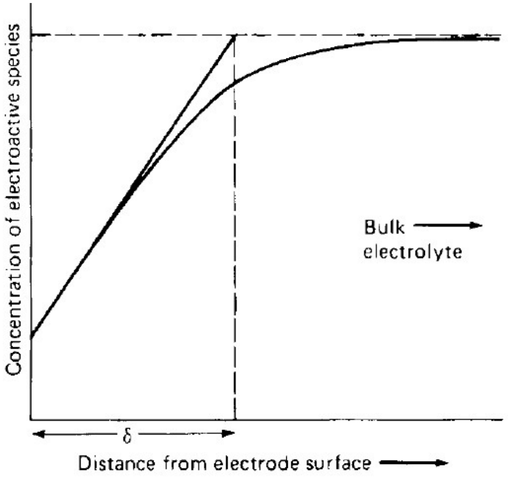
$$j = nFq$$

The dependance on ion concentration and generated current can be expressed as:

$$i = nF\frac{DA(C_B - C_E)}{\delta}$$

Where C_B is the ionic concentration within the electrolyte bulk, C_E is the concentration at the electrode, A is the electrode area, while δ is the thickness of the boundary layer at the electrode surface, where the highest ion concentration can be found. Thus, the maximum diffusion current (limiting current, i_L) is developed when $C_E = 0$:

$$i_L = nF\frac{DAC_B}{\delta_L}$$



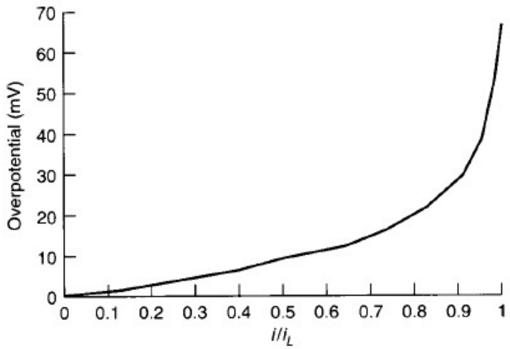
BATTERIES – CONCENTRATION POLARIZATION

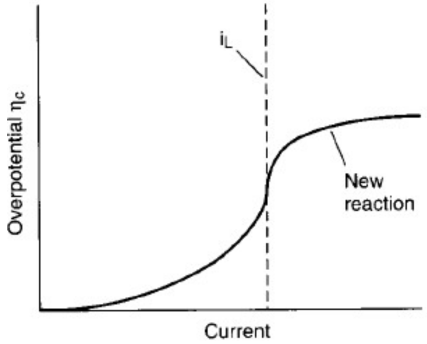
By assuming that the thickness of the diffusion boundary layer does not change much with concentration ($\delta = \delta_L$) it is possible to express the generated current as a fraction of the maximum producible one:

$$i = \left(1 - \frac{C_E}{C_B}\right) i_L$$

And, according to the Nernst equation, it is possible to relate the concentration polarization overpotential to the ion concentration ratio and to the limiting current as well:

$$\boxed{\eta_c = \frac{RT}{nF} \ln \frac{C_B}{C_E} \quad \leftrightarrow \quad \eta_c = \frac{RT}{nF} \ln \left(\frac{i_L}{i_L - i}\right)}$$





BATTERIES – TEMPERATURE INFLUENCE

The performance and aging of batteries depend critically on temperature:

- Diffusion processes slow down at low temperatures
- Side reactions can become dominant at extreme temperatures
- Certain chemical reactions, under the right conditions, can exhibit thermal runaway where the temperature increases rapidly (self-heating rates above approximately 10°C/min) and the pack can combust or explode

Temperature dependence of the reaction rate constant is usually expressed by means of the Arrhenius equation:

$$k = k_{ref}\, e^{\frac{E_{act}}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T}\right)}$$

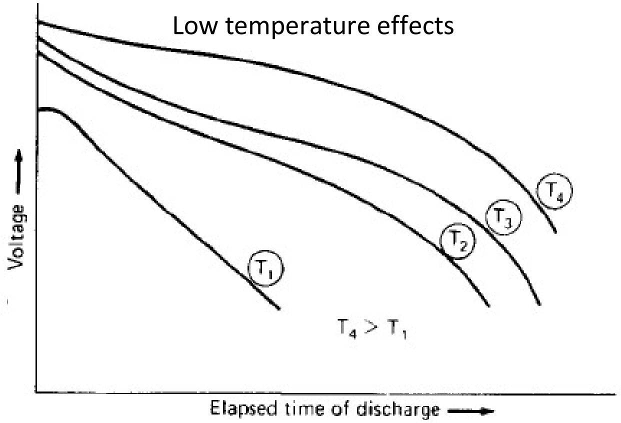
Where T_{ref} is commonly set to 25°C and k_{ref} is the reference value of the reaction rate constant at reference conditions.

Thus temperature affects the exchange current density; as seen before:

$$j_0 = \frac{i_0}{A} = nFkC_0^{(1-\alpha)}C_R^{\alpha} \rightarrow j_0 \propto k$$

BATTERIES – TESTING CONDITIONS

Temperature Batteries perform poorly at extremely low and high temperatures. At low temperature, ionic diffusion and migration can be hindered and damaging side reactions (e.g., lithium plating) can occur, resulting in reduction of chemical activity and increase of internal resistance. High temperatures favor other side reactions, such as corrosion and gas generation. Moreover, the internal resistance decreases, the discharge voltage increases and, the capacity and energy output usually increase together with chemical activity and it could lead to a rapid self-discharge processes causing a net loss of capacity. For Pb–acid batteries, charge and discharge temperatures should be limited to an operating range of -40 ÷ 60 °C. Li-ion batteries have an operating range of -20 ÷ 60 °C. Ni-MH have the narrowest operating range of -20 ÷ 45°C.


Low temperature effects

BATTERIES – TESTING CONDITIONS

Discharge mode The mode of discharge of a battery, among other factors, can have a significant effect on the battery performances due to the different characteristics which the drawn current is going to have. Discharge modes are:

1. *Constant Resistance* – The resistance of the load remains constant throughout the discharge: $I \propto V$, thus current value decreases during the discharge in proportion to the voltage decrease.

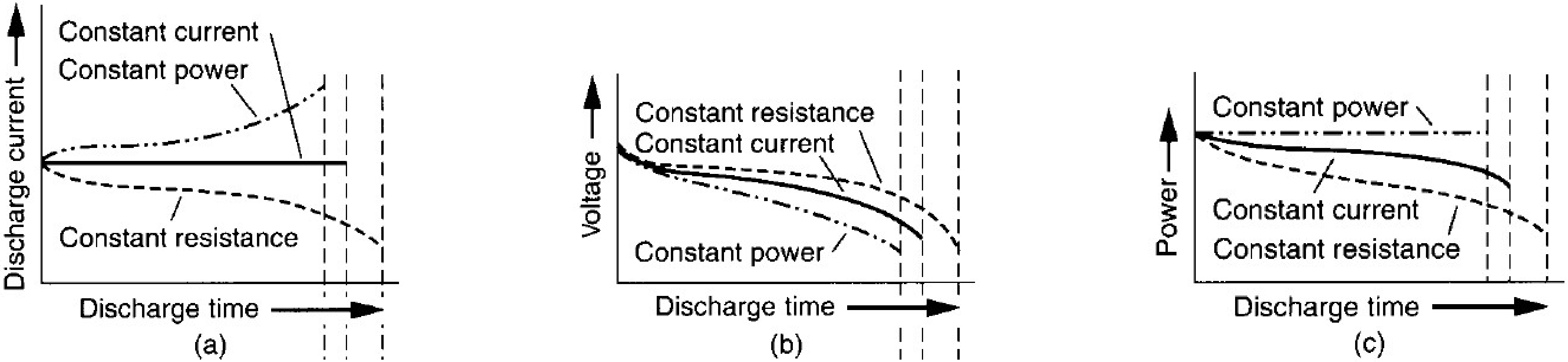
2. *Constant Current* – The current remains constant during the discharge.

3. *Constant Power* – The current increases during the discharge as the battery voltage decreases, discharging the battery at constant power level ($P = VI$).

Then, the effects of these three discharge modes can be observed in function of:

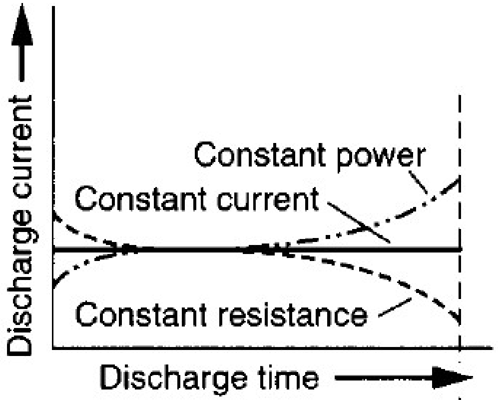
BATTERIES – TESTING CONDITIONS

- Same current and power at start of discharge

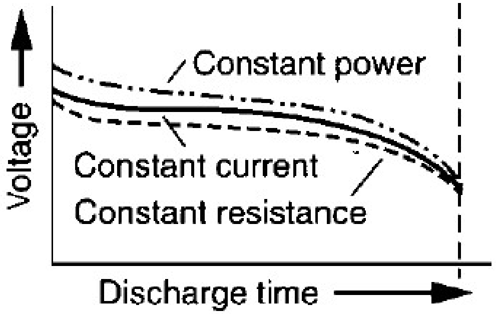


BATTERIES – TESTING CONDITIONS

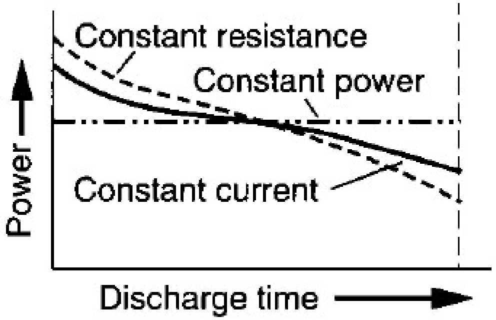
- Same discharge time



(a)



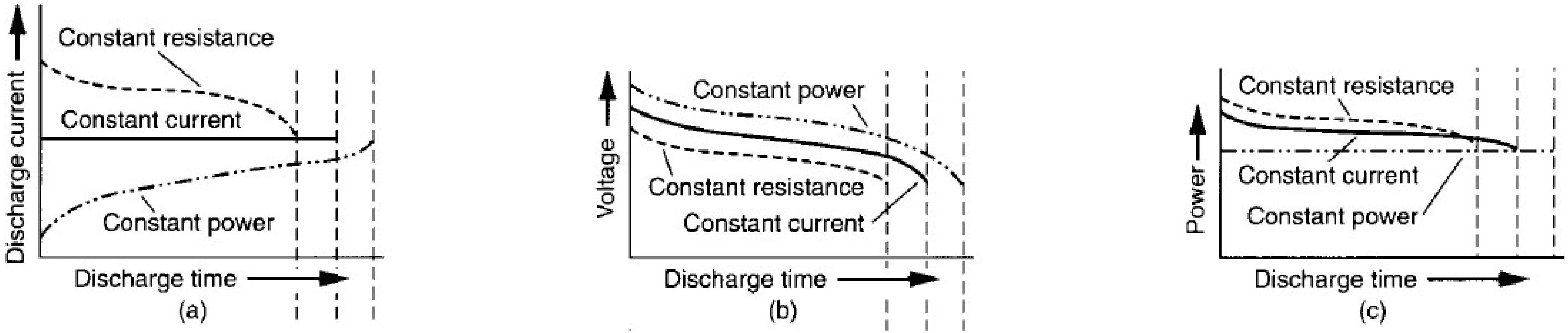
(b)



(c)

BATTERIES – TESTING CONDITIONS

- Same power at end of discharge



BATTERIES – THE STATE OF CHARGE

State of Charge The State of Charge (SOC) is defined as the percentage of the maximum possible charge that is present inside a battery. By defining the nominal capacity of a battery as the maximum amount of charge that can be drawn from the fully charged cell at room temperature and a C/30 rate, the SOC is expressed as:

$$SOC = \frac{C_r}{C} = 1 - \frac{1}{C}\int_0^t I(\tau)d\tau$$

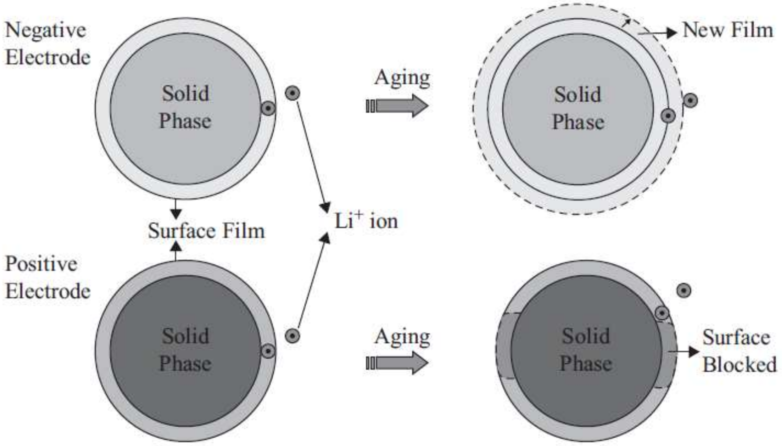
Assuming that SOC = 100% at t=0. At this point it is assumed that the battery can provide C/30 A for 30h. A complementary parameter to the SOC is the Depth of Discharge (DOD) which defines the amount of charge which has been drawn from the battery.

$$DOD = 1 - SOC$$

SOC is not directly measurable in a battery, so it must be inferred from other measurements or estimated by the battery management system. Voltage, current, and sometimes temperature are measured for this purpose in the less intrusive way.

BATTERIES – AGIGN MECHANISMS

Solid-electrolyte-interface layer growth The solid-electrolyte-interface layer grows on the negative electrode due to precipitation of unwanted reaction products, leading to an impedance rise. The solid-electrolyte-interface layer forms at the beginning of cycling and grows during cycling and storage, especially at higher temperatures. The solid-electrolyte-interface layer entrains lithium. The growing solid-electrolyte interface layer increases the cell impedance and permanently removes lithium from the cell, thus reducing capacity. Moreover, the film thickness makes change overall porosity, conductivity, and diffusion coefficients (due to precipitate of side-reaction product clogging the pores of the existing surface). Thus, the access to the active particles is restricted by the precipitate, increasing impedance and reducing the active material and cell capacity.

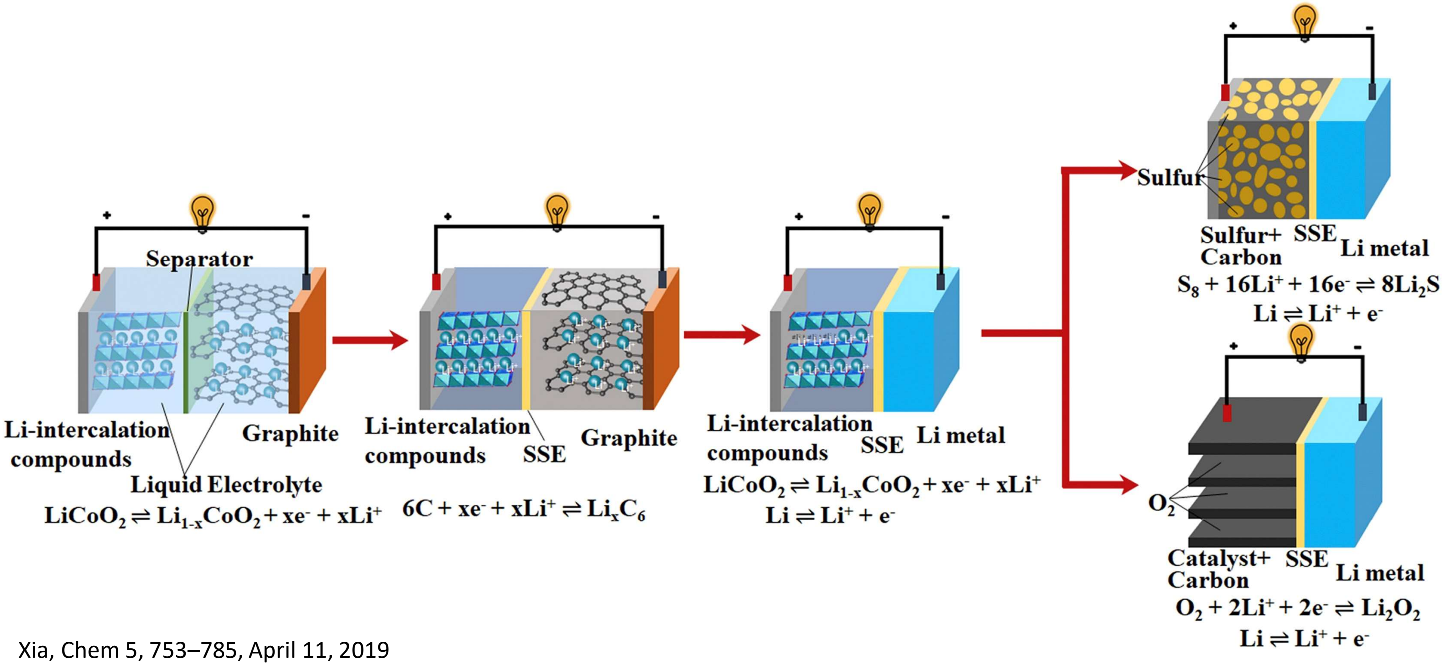


Lithium corrosion Lithium in the active carbon material of the negative electrode can corrode over time, causing capacity fade due to irreversible loss of mobile lithium.

Contact loss The solid-electrolyte-interface layer disconnects from the negative electrode, leading to contact loss and increased cell impedance.

Lithium plating Lithium metal can plate on the negative electrode at low temperatures, high charge rates, and low cell voltages, causing irreversible loss of cyclable lithium.

BATTERIES – PERSPECTIVES



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