# Basic Concepts and Conventions

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## Definitions

The following table lists the various properties and their units relevant to this chapter.

Table 2.1: Nomenclature concerning charge transport

|  |  |  |
| --- | --- | --- |
| **Name** | **Symbol** | **SI Unit** |
| Current |  |  |
| Current Density | or |  |
| Electric Potential |  |  |
| Electric Potential Difference |  |  |
| Electric Field |  |  |
| Power |  |  |
| Resistance |  |  |
| Conductance |  |  |
| Resistivity |  |  |
| Conductivity | (or ) |  |
| Molar Conductivity |  |  |
| Faraday’s Constant |  |  |
| Velocity |  |  |
| Mobility |  | or |
| Viscosity |  |  |

### Current

Current is a combination of electron flow and ion flow…electrons get converted to ions at one electrode and back to electrons at the other, but both modes are current moving.

It is defined as the number of coulombs of charge flowing per second, which is given the SI unit of amps, :

|  |  |  |
| --- | --- | --- |
|  |  | (2.1) |

### Current Density

Current is the important metric from a systems perspective (e.g. if we buy a ‘black box’ battery we only care about the current and voltage it will provide). But as engineers designing electrodes, we need a way to describe how much current is flowing ‘locally’, as illustrated in Figure 2.1. We normalize the current by the electrode area:

|  |  |  |
| --- | --- | --- |
|  |  | (2.2) |

Current “density” is analogous to heat and mass “flux” since , thus , while heat flux is and mass flux is .

### Potential or Voltage

Potential is the driving force that moves charged particles around. It analogous to pressure, or concentration. It represents an accumulation (or deficit) of charge in one location which motivates charged particles to move around in an attempt to equalize the gradients[[1]](#footnote-2).

A volt is the amount of work required to move a unit of charge between two points:

|  |  |  |
| --- | --- | --- |
|  |  | (2.3) |

### Electrical Energy and Power

If a cell operates with a total current of , at a voltage of , then power generated or expended is:

|  |  |  |
| --- | --- | --- |
|  |  | (2.4) |

Or in terms of energy consumed (or stored):

|  |  |  |
| --- | --- | --- |
|  |  | (2.5) |

Have you ever wondered what a kilowatt-hour means? If your house is burning (e.g. you have 200 LED light bulbs all on at once for some reason), then you need to pay 10-20 cents for every hour you do this.

## Sign Conventions

In a Galvanic cell where current is produced spontaneously (i.e. a battery), current flows downhill, from the positive to negative terminal. Since current flows in the opposite direction of electrons, this means that electrons flow uphill (or that they are attracted to the positive terminal and repelled by the negative one). Thus, in a Galvanic cell, where current flow is spontaneous, the anode is negative, and the cathode is positive. The opposite is true in an Electrolytic cell. This is outlined in the table below:

|  |  |  |
| --- | --- | --- |
| **Electrode / Process** | **Galvanic Cell** | **Electrolytic Cell** |
| **Cathode / Reduction** | + (e.g. Cu in Daniell Cell) | - (e.g. Zn in Daniell Cell) |
| **Anode / Oxidation** | - (e.g. Zn in Daniell Cell) | + (e.g. Cu in Daniell Cell) |

### Direction and Sign of Current Flow

Consider the cell shown in Figure 2.2. At first glance, you might say that since electrons are *produced* at the anode, then current must be *consumed* (since they flow in opposite directions) and conclude that anode current is negative; however, this neglects the fact that current also *leaves* the anode via ions, appearing to be *produced*. In fact, current is not destroyed, it just flows continuously around the circuit. So which direction is positive, and which is negative?

This conundrum can be solved as follows:

* The definition of positive and negative current flow is chosen by convention
* Because we are more interested in ions, we define the current flow by the movement of ions.
* So, the ionic current leaving the anode is taken to mean that the anode current is positive.
  + When doing a balance around the anode, the positive production of ions corresponds directly with the positive current
* We can also say that the electrode where electrons are produced corresponds to positive current
  + This is more convenient in cases where ion movements are complex

## Electrical Connections in Multi-Electrode Cells

When dealing with large scale systems, one cell is never enough.

* A typical cell has of potential, but we often want
* Or…a typical cell might produce , but we may need hundreds
* How to get this?
  + Put a bunch of cells in series, often called a ‘stack’.

The dictionary definition of the word *battery* is:

*“a number of similar articles, items, or devices arranged, connected, or used together”*

### Mono-Polar

In this arrangement, the cells are all setup in parallel as shown in Figure 2.4(left). It is called mono-polar because each plate operates at a single polarity on both sides, either positive or negative.

This gives us high current but low voltage.

Example 2.1: Calculation of power in a mono-polar arrangement

Consider the monopolar cell arrangement shown in Figure 2.4. Each electrode is a sheet, and is being applied to between anode and cathode. Find the power required if the current density is ?

**Solution**

There are 4 anodes (1 sheet with 2 sides, plus 2 sheets on each end operating only 1 side) and 4 cathodes

The total surface area is thus

The total current is thus

And the total power is

**Comment**

We could have used the cathode #’s to find current since anode and cathode currents are equal.

### Bi-Polar

This arrangement has all cells setup in series, as in Figure 2.4(right). It is called bipolar because each plate a different polarity on each side.

This gives us high voltage but low current.

Example 2.2: Calculation of power produced in a bi-polar arrangement

Consider the bipolar cell arrangement shown in Figure 2.4. Each cell in the stack is operating at a voltage drop of , and a current density of . Find the power generated.

**Solution**

The current entering one cell just moves the next, so the actual current is

There are 4 cells, and each one adds to the current, for a total of .

The total power is thus .

The bipolar arrangement is much more compact since each plate does not need its own electrical lead. This is used in fuel cells, flow batteries, and electrolyzers, as illustrated in Figure 2.5.

### Mode of Operation

It’s possible to control current or voltage, but not both. Recall from Ohm’s law that . If is fixed, then algebra dictates that we can only set one or the other.

* Setting the current, as you do in a battery, is called Galvanostatic mode
* Setting the voltage, as in a plating bath, is called Potentiostatic mode
* By analogy, you cannot set the temperature and pressure of a gas (in a closed system):

## Current Efficiency

In many cases, more than 1 reaction occurs simultaneously on a *single* electrode. These reactions occur as parallel competitive processes.

The total current is split between these reactions:

|  |  |  |
| --- | --- | --- |
|  |  | (2.6) |

where through are the amount of current for each of the various reactions occurring at the same time.

The *current efficiency* is defined as:

|  |  |  |
| --- | --- | --- |
|  |  | (2.7) |

The current efficiency refers to an electrode reaction and *not* to the entire electrochemical cell.

Example 2.3: Current Efficiency in Electrowinning

Zinc is being plated at the cathode of an electrolytic cell, however, the process is being carried out under conditions that ions in the electrolyte also combine to form gas at the cathode. The counter-reaction occurring at the anode is water splitting to make gas and . Derive an expression for the current efficiency of the two cathode reactions. The half-cell reactions are given below.

Cathode: (1) , current =

(2) , current =

Anode: (1) , current =

Overall:

**Solution**

The current efficiency of reduction at the cathode is the portion of the current dedicated to plating, divided by the total current at the cathode (or anode):

And for evolution:

**Comments**

Do we want or to be higher?

We are trying to recover zinc, so all current used on something else is a waste

What is the current efficiency at the anode?

There is only one reaction so it’s 100%.

Note that current efficiencies at the cathode and anode are not necessarily equal.

## Faraday’s Law of Electrolysis

Faraday’s Law relates the electronic charge transferred to mass or moles reacted. It is essentially a unit conversion between moles (molecules) and coulombs (electrons)

As an engineer, you want to know:

* How much current must you use to synthesize moles of chemical
* How much current will you obtain from a of anode material
* Faraday’s law is basically a unit conversion between moles and coulombs, or and

Consider the following reaction:

|  |  |  |
| --- | --- | --- |
|  |  | (2.8) |

where , and are stoichiometric coefficients, and are ionic charges (e.g. ).

Note: In an operating cell another reaction occurs at the other electrode, with a similar expression. Each of these reaction is called a “half-cell” reaction, and as usual, two halves make a whole.

We can use our knowledge of stoichiometry to derive Faraday’s law:

* Recall that Avagadro’s constant is the number of molecules in a mole,
* Number of electrons transferred to produce moles of is
* Number of electrons transferred per mole of is
* Total charge of electrons transferred per mole of produced is , where is the charge on an electron
* Total charge transferred to produce moles of is =

is a universal constant given the name “Faraday’s Constant”, :

The first form of Faradays’ law is:

|  |  |  |
| --- | --- | --- |
|  |  | (2.9) |

In the case of a normal cell, there is constant *flow* of charge, so we can write Faradays’ law as:

|  |  |  |
| --- | --- | --- |
|  |  | (2.10) |

Noting that per is current, , we can write the 2nd form of Faraday’s law:

|  |  |  |
| --- | --- | --- |
|  |  | (2.11) |

* This equation relates the molar flow rate of species , , to the actual current produced, .
* We will use Eq.(2.11) A LOT in this course. Memorize it, and consider getting it as a tattoo!

Example ‑: Applying Faraday’s law to the hydrogen oxidation reaction present in a hydrogen-air fuel cell

Develop an equation relating the stoichiometric consumption of hydrogen at the anode of a hydrogen fuel cell to the current produced.

**Solution**

The oxidation reaction is:

For this reaction, the coefficients of interest are: , , and .

Application of Faraday’s law gives:

Note the minus sign, indicating that electrons are produced as is consumed (i.e. is a negative number).

Inserting values into Faraday’s law gives:

Thus, there are 2 electrons generated for each consumed.

Alternatively, we can do the analysis on :

Note this time the positive sign, since both current and are produced.

Inserting values:

Thus, there is 1 electron generated for each generated.

**Comments**

1. When the reaction proceeds *as written*, and . Therefore, both results tell us that , as expected for an anodic reaction.
2. In a battery, the anode is the *fuel* and it spontaneously produces electrons for us to use.
3. If the reaction proceeds in the opposite direction, do we change the signs? NO! This will happen automatically due to the changing molar consumption rates.

**Example 2‑5: Applying** Faraday’s law to the oxygen reduction reaction present in a hydrogen-air fuel cell

Develop an equation relating the stoichiometric consumption oxygen at the cathode of a hydrogen fuel cell to the current produced.

**Solution**

The oxygen reduction reaction is:

The relevant stoichiometric coefficients for this reaction are: , , , and .

* Note that we treat electrons as products, so is for species on the opposite side of the electrons.
* This corresponds to the simple concept that “A goes to B”: .

Inserting numbers into Faraday’s law gives:

Thus, there are 4 electrons consumed for each consumed.

Again, we can alternatively do the analysis on :

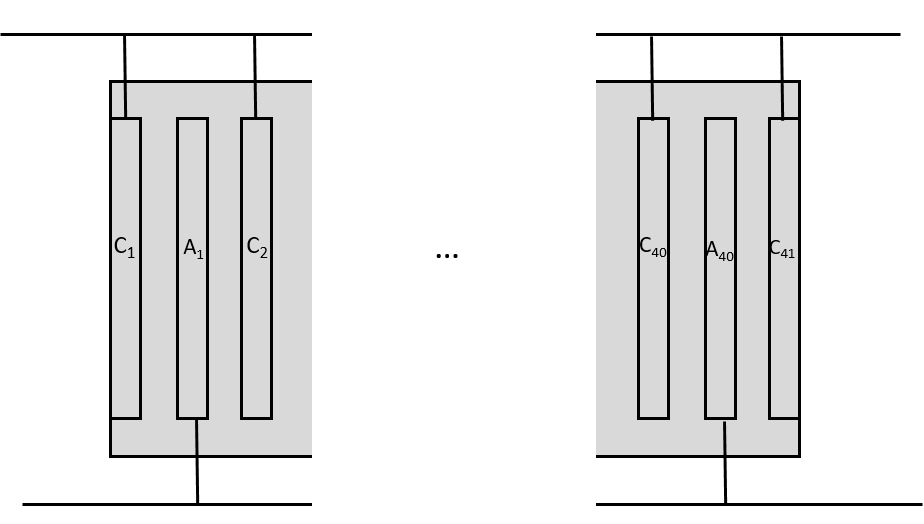
There is thus 1 electron consumed for each consumed at the cathode ( was produced at the anode)

**Comments**

1. When the reaction proceeds *as written*, and , therefore and it is a *cathodic reaction*.
2. As written, electrons are *consumed*, so this reaction would pair with an anodic reaction where electrons are *produced*.
3. This does not infer spontaneity as in a “battery”. All anodic reactions release electrons and all cathodic reaction consume electrons. This is the basis of the “red cat and an ox” pneumonic.

Example 2.6: Lead Plating in a Monopolar Stack

A lead electrorefining system is operating at an overall current density of . Each tank contains 40 anodes and 41 cathodes in a monopolar arrangement as shown below.



The electrodes are arranged in an alternating sequence of cathode and anode sheets in each tank. The last electrodes at both ends are cathodes. Lead is plated onto both sides of each cathode, except for those at the ends, which are only plated on one side.

The portion of each electrode immersed in electrolyte measures by . If the current efficiency for lead deposition is 93%, calculate the number of tanks that must be added if the aim is to produce per day. The oxidation state of dissolved lead is +2.

#### Things to Remember: Faraday’s Law Edition

1. Faraday’s law is essentially a unit conversion between and (aka amps, ), with Faraday’s constant, having units of .
2. By convention we choose anode current to be positive and cathode current to be negative. This is totally arbitrary, but we must choose something, so this is it.
3. To be consistent with the sign conventions, use the following steps when applying Faraday’s law:
   1. When writing the equation for a half-cell reaction, always write it in the anodic direction, with electrons on the RHS:
   2. Use as the stoichiometric constant for all reactants (i.e. , etc) and for all products (plus for electrons).
   3. When writing Faraday’s law for a reactant ( or ) be sure to include a negative sign:
   4. When writing it for a product ( or ) be sure to use a positive sign:
   5. This sign of will then control the final sign of the current as expected. For instance, for the reaction occurring at the anode, we can write:

and would be negative since it’s being consumed, thus canceling out the negative sign to give a positive current.

By contrast, perform the same calculation based on :

where is positive since it’s being created and hence the current is also positive.

## CSTR Model of Electrochemical Cells

Because they are still chemical reactions, we can apply the CSTR model to electrochemical cells (also known as reactors). The main assumption of the CSTR Model are:

* Perfectly mixed contents within reactor
* Concentrations are uniform throughout
* Discharge concentrations are the same as the reactor concentration
* Inlet concentration is different than reactor, but it mixes perfectly and instantly
* Temperature is also constant throughout

### Develop CSTR Equations

Consider the example of metal plating in a *monopolar* cell, with water-splitting as the counter-reaction:

|  |  |  |
| --- | --- | --- |
| **Electrode** | **Reaction** | **Current** |
| **Cathode** |  | or since there is only one reaction at cathode |
| **Anode** |  | or just since only one anode reaction |

* Do molar balances on dissolved species over entire reactor tank.
* Don’t do balances on , solid species, or gas.
* You need to include these in the balances where necessary, but you don’t need to do a balance on them
* For instance, solid metal is not flowing, so there is nothing to balance

The following table lists the various nomenclature used in the CSTR balances:

Table 2.2: Nomenclature used in CSTR balances

|  |  |
| --- | --- |
|  | concentration of in the feed |
|  | concentration in the reactor |
|  | concentration of in the feed |
|  | concentration in the reactor |
|  | volumetric flow rate of feed stream |
|  | volumetric flow rate of the outlet stream |
|  | volume of electrolyte within the reactor |
|  | steady state |

#### Transient Balance on Ions

The rate of accumulation is equal to the rate entering the tank, less the rate leaving, plus the rate any generation (or consumption) within the tank. In terms of the nomenclature defined above, this gives:

|  |  |  |
| --- | --- | --- |
|  |  | (2.12) |

* Each term in the above balance should have units of mol/s to be consistent

How do we evaluate ?

* Use Faraday’s law for the cathode reaction

Application of Faraday’s law gives:

|  |  |  |
| --- | --- | --- |
|  |  | (2.13) |

Solving for the reaction rate:

|  |  |  |
| --- | --- | --- |
|  |  | (2.14) |

Since we are consuming at the cathode during plating, and therefore . We can thus rewrite the balance as:

|  |  |  |
| --- | --- | --- |
|  |  | (2.15) |

where must be less than 0, since is being removed from the tank which is accounted for by the last term in Eq.(2.15).

#### Transient Balance on H+ Ions

A similar analysis on this species gives:

|  |  |  |
| --- | --- | --- |
|  |  | (2.16) |

Again, using Faraday’s law on the anodic reaction we can evaluate .

|  |  |  |
| --- | --- | --- |
|  |  | (2.17) |

And therefore:

|  |  |  |
| --- | --- | --- |
|  |  | (2.18) |

Since we know that at the anode, then the above result means that . And finally we have:

|  |  |  |
| --- | --- | --- |
|  |  | (2.19) |

In this case we have , since there is only one reaction occurring on each electrode and their currents must be equal and opposite.

#### Aside: Compare mono-polar and bi-polar cells

CSTR calculations must include the total current, so care must be taken to differentiate between monopolar and bipolar systems.

* and must account for rates of change in the entire reactor.

In a monopolar system:

* The total current through a monopolar reactor is the current generated at each cell added together

How would the situation change if bipolar connections were used?

* The total current through a bipolar reactor is much lower than a monopolar reactor.
* The total reaction rate is the amount of reaction (i.e. current) at one plate, multiplied by the number of plates.

Thus: and

#### Case Study: 2 cathode reactions

What are the balance equations for the following scheme:

|  |  |  |
| --- | --- | --- |
| **Electrode** | **Reaction** | **Current** |
| **Cathode** |  | or just for brevity |
|  |  | or just for brevity |
| **Anode** |  | or just since only one anode reaction |

The balance equations for a monopolar cell become for

|  |  |  |
| --- | --- | --- |
|  |  | (2.20) |

|  |  |  |
| --- | --- | --- |
|  |  | (2.21) |

|  |  |  |
| --- | --- | --- |
|  |  | (2.22) |

Note that the relationship between the currents has changed. We now have:

#### Case Study: Same species reacting at both electrodes

Consider the following reactions:

|  |  |  |
| --- | --- | --- |
| **Electrode** | **Reaction** | **Current** |
| **Cathode** |  | or for brevity |
|  |  | or for brevity |
| **Anode** |  | or since only one anode reaction |

The balance equations for a monopolar cell become:

|  |  |  |
| --- | --- | --- |
|  |  | (2.23) |

For the balance, we must be careful since it is consumed at the cathode *and* produced at the anode.

What is ?

For the cathodic reaction:

, , therefore

And for the anodic reaction:

, , therefore

Therefore:

|  |  |  |
| --- | --- | --- |
|  |  | (2.24) |

The relationship between the currents:

Example 2.7: Nickel electrorefining

Nickel electrorefining is being carried out continuously in a tank containing 61 anodes and 60 cathodes, electrically wired with monopolar connections.

The operation can be modelled as a CSTR. In this process, impure anodes are dissolved via:

, current =

And is plated to a higher purity at the cathode:

, current =

A secondary reaction also occurs at the cathode:

, current =

Only oxidation occurs at the anode.

Each cathode is plated on both sides. Each cathode is wide and is immersed to a depth of in the electrolyte.

Each anode is dissolved on both sides, except the two at the end which dissolve only on one side each. Each anode is wide and immersed to a depth of .

During the operation of the cell, the tank is continually fed by a stream containing dissolved and .

Laboratory experiments have shown a current efficiency of 95% for deposition at the cathode can be achieved if the electrolyte composition is maintained at of and pH of 4.0 throughout the electrolysis.

What must the concentration and be in the feed to ensure that can be deposited in the cell per day (assuming the lab results can be achieved at scale). The volumetric flow rate of electrolyte through the tank is . Assume solutions are ideal and the CSTR assumptions apply.

## Electroneutrality

Charge must always balance in the electrolyte. This manifests in the following features:

* If a charge is created, it must be destroyed somewhere else
* The electrolyte solution always has an equal number of + and – charges
* can be balanced by or
  + Or and (adding up to 10 units of charge)

The profile of “charge density” in the presence of an electric field can be calculated using the Poisson equation:

|  |  |  |
| --- | --- | --- |
|  |  | (2.25) |

where is the permittivity of the solution in and is assumed constant, and is the net charge density at position in . A schematic of an electric field is shown in Figure 2.8.

Since is a charge density, we can relate it to concentration (i.e. mole density) of ion using the static form of Faraday’s law:

|  |  |  |
| --- | --- | --- |
|  |  | (2.26) |

where is the charge on species , is the concentration of species at the location . Written this way we can see that has unit of . We find the total charge density, , by summing Eq.(2.26) for all species:

|  |  |  |  |
| --- | --- | --- | --- |
|  |  |  |  |

* The concentration of charge at a location is proportional to the concentration of ions, which are charged particles
* We must account for the charge on each ionic species, and convert moles to coulombs

We can now substitute Eq.(2.26) in for the charge density to get:

|  |  |  |
| --- | --- | --- |
|  |  | (2.27) |

If we were to integrate this equation for we could find the concentration profile across the cell arising from the presence of an electric field. As shown schematically in Figure 2.9, this is very flat line.

This is because we are taking the second derivative of the voltage field, so the rate of (rate of change) is nearly constant.

If the assumption of electroneutrality is valid, we can generally write:

|  |  |  |
| --- | --- | --- |
|  |  | (2.28) |

This equation states that the total charges at location cancel out, or sum to zero.

This equation will be used later to justify neglecting of convective mass transfer

Note: This assumption is not valid over very short distances (). The accumulation of charged particles near the surface of the electrode results in the situation shown in Figure 2.10.

* Only occurs within of a charged surface or ion
* This is called the Helmholz double layer
* This is crucial to electrochemical supercapacitors
* Also, worth thinking about when studying catalysts
* But is not of any practical importance to the engineering applications we’ll be focusing on

## Figures

|  |
| --- |
| Figure 2.1: Pictorial definition of current density |

|  |
| --- |
| Figure 2.2: The Daniel cell has a negative zinc and positive copper electrode. In galvanic mode the current flow counter-clockwise (opposite direction to electrons). |

|  |
| --- |
| Figure 2.4: Schematics of mono-polar (middle) and bi-polar (right) cell arrangements |

|  |
| --- |
| Figure1-FuelCellConstruction.jpg  Figure 2.5: Schematic diagram of a fuel cell stack with bipolar plates separating each “MEA” |

|  |
| --- |
| Figure 2.6: Illustration of current efficiency in zinc-plating where some of the total current is diverted to the evolution reaction |

|  |
| --- |
| Figure 2.7: Schematic of a basic CSTR familiar to chemical engineers |

|  |
| --- |
| Figure 2.8: Profile of electric field strength across a dielectric material, such as water |

|  |
| --- |
| Figure 2.9: Profile of ionic species concentration across cell in the presence of an electric field |

|  |
| --- |
| Figure 2.10: Schematic representations of the ‘double’ layer. Left if the basic Helmholtz model and right shows the more realistic Gouy-Chapman model which includes randomness induced by thermal motion. |

1. There is a very interesting short story by a famous sci-fi writer named Ted Chiang, called Exhalation. This story is about pneumatically powered robots living inside a sealed dome. One robot realizes that the pressure inside the dome is slowly rising and will eventually match that outside the dome, at which point they will cease to function because there will be no more driving force. This is the best analogy I know of for thermodynamics, entropy, and voltage. [↑](#footnote-ref-2)