# DETERMINATION OF DONNAN MEMBRANE POTENTIALS AND LIQUID-JUNCTION POTENTIALS

**General Schedule and Comments** *(this text is the same as was presented for Lab 2)*

In general, the format for this discussion session will be the same each week and is as follows:

1. Briefly review the experiments, their goals, and any updates to the hands-on activities
2. Break into groups of two or three, set-up each workspace, and make a connection between a laptop running Windows and the BioLogic potentiostat using the EC-Lab software
3. Perform experimental procedure(s), while being assisted by the Instructor
4. If time permits, as a class provide feedback on the activity and recommend future changes
5. Clean-up each workspace, return items used, and store electrodes for subsequent weeks *(You are not dismissed from the discussion session until this is complete)*

*It is recommended that you read through and save and/or print procedures and reference publications/files before you watch the experimental pre-lab video and attend the hands-on discussion sessions. This will help you to become acquainted with the experiment and formulate questions to ask during the discussion session. Being interactive with the videos (e.g. by actively asking yourself questions as to why the experiment is set up in a certain way, why data looks the way it does, etc.) will help to increase your knowledge and comfort with the techniques shown. This will then help you to successfully complete homework assignments and implement techniques in your own research.*

## Introduction

Thus far in the hands-on discussion sessions you have "applied" and measured potentials between a working electrode and a reference electrode. *(The reason for the use of "applied" is that the wall outlet actually powered the application of a bias at the counter electrode versus virtual ground but we report all values as the potential observed between the working electrode and the reference electrode.)* You have also measured the open-circuit potential ($E_{oc}$), while not intentionally passing much current, where in fact, only two electrodes would have sufficed or even simply a voltmeter. In those previous experiments, $E_{oc}$ was dominated by the difference in the Nernst potentials that report on the electric potential difference across the interfacial double layer at the working electrode and at the reference electrode. This week you will perform experiments that illustrate how measuring $E_{oc}$ can report on more than just Nernst potentials, but also any electric potential differences across interfaces between electrolytes and/or membranes in the ionic circuit, as well as in their bulk. This occurs because when one measures $E_{oc}$, a small amount of current must pass between the working electrode and reference electrode (on the order of femtoamps in BioLogic potentiostats) and, due to Kirchhoff's current law, this includes ion transport in solution by migration that results in ions charging and/or crossing all interfaces and bulk phases.

**Purpose**

The purpose of this hands-on discussion activity is to become more familiar with scenarios where liquid-junction potentials and Donnan potentials are large. Before the activity starts, ~1 M counter-ions present in commercial ion-exchange membranes will have been exchanged with specific ions: (1) for one piece of Nafion 212 cation-exchange membrane (*protonated*), we introduce cationic protons as counterions to its covalently bound anionic sulfonate groups; (2) for a second piece of Nafion 212 cation-exchange membrane (*potassiated*), we introduce cationic potassium ions as counterions to its covalently bound anionic sulfonate groups; and (3) for one piece of Sustainion X37, or other anion-exchange membrane (*chloridated*), we introduce anionic chlorides as counterions to its covalently bound cationic imidazolium groups. Then, using the *protonated* Nafion membrane, you will determine (Type 1 / Donnan) liquid-junction potentials that arise due to a difference in the concentration of aqueous acid (HCl) that wets each side of the membrane, followed by measurement of (Type 2) liquid-junction potentials that arise due to a difference in the concentration of aqueous cations that wet each side of the membrane. Then, you will repeat the (Type 1 / Donnan) liquid-junction potential measurements using different concentrations of aqueous base (KOH) that wets each side of the membrane, specifically, the *potassiated* cation-exchange membrane, followed by a similar series of measurements using different concentrations of aqueous acid (HCl) that wets each side of the, specifically, *chloridated* anion-exchange membrane.

**Safety**

For each hands-on discussion session, you must bring and wear personal protective equipment consisting of a lab coat and safety glasses/goggles. In addition, at a minimum you must wear closed-toe shoes, pants, and a shirt that covers your entire torso, or else you will not be allowed to enter the lab. While in the lab you will also need to wear gloves, which we will supply as nitrile gloves. In addition, to reduce the possibility of electric shock to you and your labmates be sure to control the correct channel of the potentiostat and that all persons are away from the experimental apparatus before starting an electrochemical experiment. *Moreover, you should never touch any of the electrodes while the potentiostat is applying a potential bias, especially the counter electrode.* Caution: All acidic and alkaline solutions should be prepared and poured in a *fume hood*. Also, observe caution with dissolution of solid KOH since it is an exothermic process, thus giving off heat, and concentrated KOH is caustic. *Note that to facilitate safety and best-use of time the Instructor may prepare all or some of the membrane pretreatments and solutions indicated below before the hands-on discussion session. The Instructor will also bring extra PPE.*

**Procedures**

Part A: Ion exchanging hydrogen/potassium ions into cation-exchange membranes and chloride ions into an anion-exchange membrane

**Tools/materials needed**: 3 beakers (each ~10 mL), 3 scintillation vials (each 25 mL and prerinsed), 2 commercial Nafion 212 membranes (or any cation-exchange membranes; each ~1 cm x 1 cm), 1 Sustainion X37 membrane (or any anion-exchange membrane; ~1 cm x 1 cm), aqueous 1 M HCl, aqueous 1 M KOH, high-purity water, sodium bicarbonate for neutralizing solutions and possible spills

(1) Remove the possibly ***two*** protective plastic coatings that sandwich each cation-exchange membrane and the possibly ***one*** protective plastic coating that supports the anion-exchange membrane. *Notably, both membranes have a thick plastic support and Nafion also has a crinkly plastic coating, which are each sometimes difficult to see and/or remove. To facilitate separation, lightly wet each membrane with water, which will cause it to swell and begin to delaminate from the plastic coatings, which may be invisible by eye.*

(2) Submerge one cation-exchange membrane into aqueous 1 M HCl for ~15 minutes† *(or as long as it takes you to set up the experiment below that needs this membrane)* to exchange the native counterions (likely protons) with protons, just in case there are impurities.

(3) Submerge the other cation-exchange membrane into aqueous 1 M KOH for ~15 minutes† *(or as long as it takes you to set up the experiment below that needs this membrane)* to exchange the native counterions (likely protons) with potassium ions.

(4) Submerge the anion-exchange membrane into aqueous 1 M HCl for ~15 minutes† *(or as long as it takes you to set up the experiment below that needs this membrane)* to exchange the native counterions (likely bromides) with more redox-inert chloride ions.

(5) After ion exchange, wash each membrane thoroughly with high-purity water to remove excess ions and store each membrane in a separate vial filled with high-purity water.

† Complete ion exchange of ion-exchange membranes typically requires upwards of 24 hours using a large volume of solution that is often stirred, heated, and replaced at least once during the process, which is ideal, but not entirely necessary for this activity.

<u>Part B: Determining Donnan potentials across cation-exchange-membrane interfaces and liquid-junction potentials within "frits" formed due to acid</u>

**Tools/materials needed**: *either* (a) a voltmeter or (b) a potentiostat, *either* (*i*) a two-cuvette electrochemical cell and a small C-clamp or (*ii*) a two-component H-cell with flanges and a small pinch clamp, Parafilm, scissors, hole punch, ***protonated cation-exchange membrane***, *2 Ag/AgCl wires and 2 separate "fritted" tubes containing aqueous saturated* ***KCl***, aqueous solutions of HCl (containing each of 0.1 mM, 1 mM, 10 mM, and 100 mM)

(1) Sandwich the *protonated* cation-exchange membrane – *that was thoroughly rinsed with high-purity water* – between the two halves of the cell including, between each membrane|cell interface, a piece of Parafilm (approximately the same size as the membrane

and with a hole punched out in its middle). Working with a partner, clamp the cell together, lining up all four holes as best as you can.

(2) Perform OCV measurements for ~1 minute each, recording the potential every second if you are using a potentiostat, and using the following aqueous concentrations of HCl in each cell compartment. *Ensure that bubbles do not completely prevent the solutions from wetting the membrane.*

| Measurement | Compartment 1, HCl | Compartment 2, HCl |
|---|---|---|
| B$^{\#}$1 / B*1 | 100 mM | 100 mM |
| B$^{\#}$2 / B*2 | " | 10 mM |
| B$^{\#}$3 / B*3 | " | 1 mM |
| B$^{\#}$4 / B*4 | " | 0.1 mM |

Perform each of these 4 Measurements twice, once each using the following reference electrode configurations **in the order indicated here**, and making sure to *thoroughly rinse the Ag/AgCl wires and Compartment 2 with high-purity water between each measurement to remove excess salt species*: $^{\#}$ immerse the *Ag/AgCl wires* directly into the aqueous HCl electrolytes, **followed by *** immerse the Ag/AgCl wires *into the "fritted tubes" containing aqueous saturated KCl* and *gently* immerse these into the aqueous HCl electrolytes so that they do not touch the membrane or agitate the solution much.

**For Measurement B$^{\#}$1 / B*1, and thus each of condition $^{\#}$ and *, first measure the OCV with both electrodes in one compartment to assess whether they have similar Nernst potentials**; indicate this condition as A$^{\#}$1 / A*1.

Part C: Determining liquid-junction potentials within and near a cation-exchange membrane formed due to various salts

**Tools/materials needed**: *either* (a) a voltmeter or (b) a potentiostat, *either* (*i*) a two-cuvette electrochemical cell and a small C-clamp or (*ii*) a two-component H-cell with flanges and a small pinch clamp, Parafilm, scissors, hole punch, ***protonated cation-exchange membrane***, *2 "fritted" aqueous Ag/AgCl (saturated with **KCl**) reference electrodes*, aqueous solutions of 100 mM salt (containing each of HCl, KOH, KCl, and NaCl)

- Using the *protonated* cation-exchange membrane from part B, repeat the experiments in **Part B*, step 2 for condition * only**, using the following aqueous concentrations of salt in each cell compartment.

| Measurement | Compartment 1 | Compartment 2 |
|---|---|---|
| C*1 | 100 mM HCl | 100 mM KOH |
| C*2 | " | 100 mM KCl |
| C*3 | 100 mM NaCl | " |

Part D: Determining Donnan potentials across cation-exchange-membrane interfaces formed due to "base"

**Tools/materials needed**: *either* (a) a voltmeter or (b) a potentiostat, *either* (*i*) a two-cuvette electrochemical cell and a small C-clamp or (*ii*) a two-component H-cell with flanges and a small pinch clamp, Parafilm, scissors, hole punch, ***potassiated* cation-exchange membrane**, *2 "fritted" aqueous Ag/AgCl (saturated with **KCl**) reference electrodes*, aqueous solutions of KOH (containing each of 0.1 mM, 1 mM, 10 mM, and 100 mM)

- Using the *potassiated* cation-exchange membrane, repeat the experiments in **Part B*, step 2 for condition * only**, using the following aqueous concentrations of base in each cell compartment.

| Measurement | Compartment 1, KOH | Compartment 2, KOH |
|---|---|---|
| D*1 | 100 mM | 100 mM |
| D*2 | " | 10 mM |
| D*3 | " | 1 mM |
| D*4 | " | 0.1 mM |

Part E: Determining Donnan potentials across anion-exchange-membrane interfaces formed due to "acid"

**Tools/materials needed**: *either* (a) a voltmeter or (b) a potentiostat, *either* (*i*) a two-cuvette electrochemical cell and a small C-clamp or (*ii*) a two-component H-cell with flanges and a small pinch clamp, Parafilm, scissors, hole punch, ***chloridated* anion-exchange membrane**, *2 "fritted" aqueous Ag/AgCl (saturated with **KCl**) reference electrodes*, aqueous solutions of HCl (containing each of 0.1 mM, 1 mM, 10 mM, and 100 mM)

- Using the *chloridated* anion-exchange membrane, repeat the experiments in **Part B*, step 2 for condition # and *** – and in that order – using the following aqueous concentrations of acid in each cell compartment.

| Measurement | Compartment 1, HCl | Compartment 2, HCl |
|---|---|---|
| E#1 / E*1 | 100 mM | 100 mM |
| E#2 / E*2 | " | 10 mM |
| E#3 / E*3 | " | 1 mM |
| E#4 / E*4 | " | 0.1 mM |

**Assignment 4 – Lab 6** *(combined with next week's activity; due on Wednesday, December 2, 2026 at noon)* (You must show your work for credit on all problems.)

1. Either using the data provided to you for Lab 6, or your own data if your laboratory experiments were successful, do the following.
   - **a.** Part B: Acid-Generated Donnan Potential Data
     - **i.** Which ion(s) dominated formation of the measured electric potential differences *and* why were cell potentials measured between fritted reference electrodes about half as large as those measured between Ag/AgCl wires?

**ii.** For *each* of the 4 electrolyte conditions (B1 – B4), calculate the *theoretical* total contributions of interfacial Donnan electric potential differences across the membrane, *and* the *theoretical* electrochemical potential difference for $H^+$ *and* $Cl^-$ across the membrane.

**iii.** For *each* of the Donnan potentials that you just calculated in *part ii*, indicate why analogous values that you measured experimentally *using the fritted reference electrodes* may have differed.

**iv.** Most cation-exchange membranes have ~1 M sulfonate groups in their hydrated regions, and thus assuming that all relevant activity coefficients equal one, calculate *for the last electrolyte condition (B4)* the *theoretical* concentration of $Cl^-$ in the hydrated membrane regions at *each* membrane|solution interface.

**b.** Part C: Salt-Generated Liquid-Junction Potential Data

**i.** Which ion(s) dominated formation of the measured electric potential differences *and* were the cells under steady-state or equilibrium conditions?

**ii.** For *each* of the 3 electrolyte conditions (C1 – C3), calculate the *theoretical* total contributions of liquid-junction electric potential differences across the membrane.

**c.** Part D: "Base"-Generated Donnan Potential Data

**i.** For *each* of the 4 electrolyte conditions (D1 – D4), calculate the *theoretical* total contributions of interfacial Donnan electric potential differences across the membrane.

**d.** Part E: "Acid"-Generated Donnan Potential Data

**i.** Which ion(s) dominated formation of the measured electric potential differences *and* why were cell potentials measured between Ag/AgCl wires immersed directly into the liquid electrolyte solutions close to zero?