

## DETERMINATION OF DONNAN MEMBRANE POTENTIALS AND LIQUID-JUNCTION POTENTIALS

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

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

1. Present brief outline of experiments, goals, and updates
2. Break into groups of two or three, set-up work space, and connect to the BioLogic potentiostat using the EC-Lab software on a PC laptop
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 other activities
5. Clean-up work space, return items, 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 the procedures and reference publications/files before you watch the experiment 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 (i.e. by actively asking yourself questions as to why the experiment is set up in a certain way and why data looks the way it does, etc.) will increase your knowledge and comfort with the techniques shown. This will help with completion of homework assignments and allow you to implement techniques in your own research.*

### Introduction

Thus far in the hands-on discussion sessions you have seen how we “apply” and measure potentials between a working electrode and a reference electrode. (The reason for the use of “apply” is that the wall outlet actually powered the application of a bias at the counter electrode versus 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 any 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 dictated the potential of the working electrode and the potential of 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. 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.

## 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 (*protonated*), we introduce cationic protons as counter-ions to its covalently bound anionic sulfonate groups; (2) for a second piece of Nafion 212 (*potassiated*), we introduce cationic potassium ions as counter-ions to its covalently bound anionic sulfonate groups; and (3) for one piece of Sustainion X37 (*chloridated*), we introduce anionic chlorides as counter-ions 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 acid (HCl) on each side of the membrane, followed by measurement of (Type 2) liquid-junction potentials that arise due to a difference in the concentration of cations on each side of the membrane. Then, you will repeat the (Type 1 / Donnan) liquid-junction potential measurements using different concentrations of base (KOH) on each side of, specifically, the *potassiated* Nafion membrane, followed by a similar series of measurements using different concentrations of acid (HCl) on each side of, specifically, the *chloridated* Sustainion 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 tee-shirt that covers your entire torso. While in 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, do not touch the electrodes while a potential bias and/or an electronic current is being applied between them, especially the counter electrode. Caution: All acidic and alkaline solutions should be prepared in a *fume hood*. Also, observe caution with KOH dissolution as it is an exothermic process, thus giving off heat, and concentrated KOH is caustic. Also, NO<sub>x</sub> fumes are toxic and HNO<sub>3</sub> is highly corrosive to tissue.

## Procedures

Part A (prepared by your Instructor before the hands-on discussion session; reported here for informative purposes): Ion exchanging hydrogen/potassium ions into cation-exchange membranes and chloride ions into an anion-exchange membrane

**Tools/materials needed:** two 50 mL beakers, two 1 cm x 1 cm commercial Nafion 212 membranes, one 1 cm x 1 cm Sustainion X37 membrane, aqueous 1 M HCl, aqueous 1 M KCl, high-purity water

- (1) Remove the **two** protective plastic coverings that sandwich each Nafion membrane and the **one** protective plastic coating that supports the Sustainion membrane: both membranes have a thick plastic support and Nafion also has a hard and crinkly plastic coating. Separation of both plastic coverings from the Nafion membrane is often challenging. To facilitate separation, lightly wet the Nafion membrane with water, which will cause it to swell and begin to delaminate from the plastic coverings, which will be clear by eye.
- (2) Submerge one Nafion membrane into aqueous 1 M HCl for ~15 minutes<sup>†</sup> (*or as long as it takes you to set up the experiment below that needs this membrane*) to exchange the native counter-ions (likely protons) for protons, just in case there are impurities.
- (3) Submerge the other Nafion membrane into aqueous 1 M KOH for ~15 minutes<sup>†</sup> (*or as long as it takes you to set up the experiment below that needs this membrane*) to exchange the native counter-ions (likely protons) for potassium ions.
- (4) Submerge the Sustainion membrane into aqueous 1 M HCl for ~15 minutes<sup>†</sup> (*or as long as it takes you to set up the experiment below that needs this membrane*) to exchange the native counter-ions (likely chlorides) for chloride ions, just in case there are impurities.
- (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.

<sup>†</sup> Complete ion-exchange of ion-exchange membranes typically requires upwards of 24 hours with stirring and often heating, which your Instructor likely did for you.

### Part B: Determining Donnan potentials across a cation-exchange membrane and liquid-junction potentials across “frits” formed due to acid

**Tools/materials needed:** Either (a) two-cuvette electrochemical cell and small clamps or (b) an H-cell; *two Ag/AgCl wires and two separate “fritted” tubes containing aqueous saturated KCl*, Parafilm, **protonated Nafion**, scissors, hole punch, aqueous solutions of HCl (100 mM, 10 mM, 1 mM, 0.1 mM)

- (1) Sandwich a protonated Nafion membrane – *that was thoroughly rinsed with high-purity water* – in the cell, with two pieces of Parafilm (same size as the membrane; hole punched out) each placed on one side of the membrane, and where the holes line up across the Nafion membrane. Clamp the cell together.
- (2) Perform OCV measurements for ~1 minute each, recording the potential every second, and using the following concentrations of aqueous HCl on each side of the Nafion membrane. Perform this measurement twice per concentration, once each using the following reference electrode configurations **in the order here**, and making sure to *thoroughly rinse the wires and compartment #2 with high-purity water between each measurement in order to rinse*

*off excess salt species:* (i) immerse the Ag/AgCl wires directly into the aqueous HCl electrolytes, **followed by** (ii') 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.

Measurement #	Compartment #1, HCl	Compartment #2, HCl
B/B'1	100 mM	100 mM
B/B'2	"	10 mM
B/B'3	"	1 mM
B/B'4	"	0.1 mM

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

**Tools/materials needed:** Either (a) two-cuvette electrochemical cell and small clamps or (b) an H-cell; *two "fritted" aqueous Ag/AgCl (saturated with KCl) reference electrodes*, Parafilm, *protonated Nafion membrane*, scissors, hole punch, aqueous solutions of 100 mM salt (HCl, KOH, KCl, NaCl)

- Using your *protonated* Nafion membrane from part B, repeat the experiments in **Part B, 2, ii** only for the following aqueous concentrations of salt on each side of the Nafion membrane.

Measurement #	Compartment #1	Compartment #2
C1	100 mM HCl	100 mM KOH
C2	"	100 mM KCl
C3	100 mM NaCl	"

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

**Tools/materials needed** Either (a) two-cuvette electrochemical cell and small clamps or (b) an H-cell; *two "fritted" aqueous Ag/AgCl (saturated with KCl) reference electrodes*, Parafilm, *potassiated Nafion membrane*, scissors, hole punch, solutions of KOH (100 mM, 10 mM, 1 mM, 0.1 mM)

- Using your *potassiated* Nafion membrane, repeat the experiments in **Part B, 2, ii** only for the following aqueous concentrations of base on each side of the Nafion membrane.

Measurement #	Compartment #1, KOH	Compartment #2, KOH
D1	100 mM	100 mM
D2	"	10 mM
D3	"	1 mM
D4	"	0.1 mM

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

**Tools/materials needed:** Either (a) two-cuvette electrochemical cell and small clamps or (b) an H-cell; *two Ag/AgCl wires and two separate "fritted" tubes containing aqueous saturated KCl*,

Parafilm, *chloridated Sustainion membrane*, scissors, hole punch, aqueous solutions of HCl (100 mM, 10 mM, 1 mM, 0.1 mM)

- Using your *chloridated Sustainion membrane*, repeat the experiments in **Part B, 2, i and ii'** – in that order – for the following aqueous concentrations of acid on each side of the Sustainion membrane.

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

**Assignment 4 – Lab 6** (*combined with next week's activity; due on Monday, November 27, 2023 at noon*) (You must show your work for credit on all problems.)

- Using the data provided to you for Lab 6, or your own data if your laboratory experiments were successful, do the following.
  - Part B: Acid-Generated Donnan Potential Data
    - Which ion(s) dominated formation of the measured electric potential differences *and* why were potentials measured between fritted reference electrodes about half as large as those measured between Ag/AgCl wires?
    - For *each* of the four conditions studied (B/B'1 – 4), calculate the theoretical total electric (Donnan) equilibrium potential across the membrane and the electrochemical potential difference for  $H^+$  *and*  $Cl^-$  across the membrane.
    - For *each* of the four conditions studied (B'1 – 4), calculate the difference between the theoretical total Donnan potentials (*from part ii*) and the experimental electric potentials measured between fritted reference electrodes and indicate what is a likely cause of any differences in these values.
    - Nafion has ~1 M sulfonate groups in its hydrated regions, and assuming all relevant activity coefficients equal one, calculate the theoretical concentration of  $Cl^-$  in the hydrated regions on *each side* of Nafion under the last condition studied (B/B'4).
  - Part C: Salt-Generated Liquid-Junction Potential Data
    - Which ion(s) dominated formation of the measured electric potential differences *and* were the cells under steady-state or equilibrium conditions?
    - For *each* of the three conditions studied (C1 – 3), calculate the theoretical electric (liquid-junction) potential across the membrane.
  - Part D: "Base"-Generated Donnan Potential Data
    - For *each* of the four conditions studied (D1 – 4), calculate the theoretical total electric (Donnan) equilibrium potential across the membrane.
  - Part E: "Acid"-Generated Donnan Potential Data
    - Which ion(s) dominated formation of the measured electric potential differences *and* why were the potentials measured between Ag/AgCl wires immersed directly into the electrolyte solutions close to zero?