DETERMINATION OF DONNAN AND LIQUID-JUNCTION MEMBRANE POTENTIALS

General Schedule and Comments (this text is the same text that was in the Lab 2 document)

In general, the format for this class 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 Bio-Logic potentiostat using the EC-Lab software on a PC laptop
3. Perform experimental procedure(s), while being assisted by the TA and the Professor
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 section until this is complete.)

Since your discussion section is short (110 minutes) and we want to cover as much as possible, please use your time wisely by getting started promptly and working efficiently. NOTE: You will need to save or print procedures and reference publications/files before you attend the hands-on discussion sections. This will help you to become acquainted with the experiments and more importantly, will allow you to stay connected to the potentiostat as you run the experiments, because there are sometimes issues when the Internet and the potentiostat are used simultaneously.

Introduction

Thus far in this course 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 ground but we report all values as the potential observed between the working electrode and the reference electrode.) To measure the open-circuit potential ($E_{oc}$) while not intentionally passing any current two electrodes would have sufficed, and where $E_{oc}$ values are 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 only measure $E_{oc}$ values between two nominally identical Ag/AgCl reference electrodes so that somewhat small electric potential drops/differences across interfaces between electrolytes and membranes can be measured.

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. First, you will exchange the ~1 M counter-ions present in commercial ion-exchange membranes with specific ions: (1) for one piece of Nafion 212 (protonated), you will introduce cationic protons as counter-ions to its covalently bound anionic sulfonate groups; (2) for a second piece of Nafion 212 (potassiated), you will
introduce cationic potassium ions as counter-ions to its covalently bound anionic sulfonate groups; and (3) for one piece of Sustainion X37 (chloridated), you will introduce anionic chlorides as counter-ions to its covalently bound cationic imidazolium groups. While this is happening you will prepare two nominally identical Ag/AgCl working electrodes by remaking and/or constructing them. 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

To each hands-on discussion section you must bring 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. Attendance at these hands-on discussion sections are mandatory so please do not get a grade of a zero due to improper lab attire. While in lab you will 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 you are working on the correct channel of the potentiostat and that all persons are away from the experimental apparatus before starting an electrochemical experiment.

Procedures

Part A: 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 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.

(2) Submerge one Nafion membrane into aqueous 1 M HCl for ~15 minutes† (as long as it takes you to do Part B below) to exchange the native (likely protons) counter-ions for protons.
(3) Submerge the other Nafion membrane into aqueous 1 M KOH for ~15 minutes† (as long as it takes you to do Part B below) to exchange the native (likely protons) counter-ions for potassium ions.

(4) Submerge the Sustainion membrane into aqueous 1 M HCl for ~15 minutes† (as long as it takes you to do Part B below) to exchange the native (likely chloride) counter-ions for 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 with stirring and often heating.

Part B: Constructing Silver – Silver Chloride Reference Electrodes – copied from Lab 2

Tools/materials needed: high-purity water, aqueous 1 M KCl or household bleach, silver wire, sandpaper, wire cutters, another electrode from above, cleaned scintillation vial, 1 mL plastic syringe, small cork, agarose, 250 mL Erlenmeyer flask, 250 mL beaker

(1) Prepare two (2) Ag/AgCl reference electrodes per the following procedure.

(2) If not already prepared by your TA, as a class prepare fitted reference electrode tubes.

a. Into a clean 250 mL Erlenmeyer flask pour ~50 mL of high-purity water and add 1 g of agarose (~2% w/w).

b. Dissolve the agarose by microwaving the mixture for 1 min on a high setting.

c. Remove the plungers and cut off the top “wings” from 20 plastic syringes (1 mL).

d. In a clean 250 mL beaker place the plastic syringes in an upright position so that the tips of the syringes are touching the base of the beaker.

e. Pour the 2% agarose solution into the beaker containing the syringes, so that all syringes are filled to the 0.2 mL mark with the agarose solution.

f. Wait approximately 20 min for the agarose solution to turn into a gel, which serves as the frit for ion transport.

(3) Take the silver wire (~6 cm in length) and clean it by sanding lightly. Then, rinse the electrode with water.

(4) Set-up a two-electrode electrochemical cell in the pre-rinsed vial to chloridize the silver wire using one of the other electrodes that you made and a chloride-containing solution (either aqueous 1 M KCl or aqueous 5% hypochlorite). Apply a potential bias sufficiently large to chloridize the electrode (90 sec at 4 V should suffice).

(5) Take one fritted plastic syringe prepared above and fill it with aqueous 1 M KCl solution.

(6) Do not yet place the visibly chloridized Ag wire in the solution, such that the chloridized end is in contact with the solution and uncoated Ag end is sticking out from the top of the syringe (this end will be used to make electrical contact with the potentiostat reference
electrode lead). Later you will plug the top of the syringe with a small cork to prevent electrolyte from leaking, but allow the Ag wire to stick out at the edge.

Be sure not to contaminate the silver with dirty gloves (e.g. oils or grease) or by placing it on surfaces (i.e. dust) as it can impede the chloridizing reaction.

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

Tools/materials needed: two-cuvette electrochemical cell, small clamps, two Ag/AgCl wires and two separate “fritted” tubes containing aqueous saturated KCl, pipe cleaners and/or paper clips, 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* – between the two cuvettes, 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 cuvettes to hold 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.

<table>
<thead>
<tr>
<th>Measurement #</th>
<th>Compartment #1, HCl</th>
<th>Compartment #2, HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>C/C'1</td>
<td>100 mM</td>
<td>100 mM</td>
</tr>
<tr>
<td>C/C'2</td>
<td>&quot;</td>
<td>10 mM</td>
</tr>
<tr>
<td>C/C'3</td>
<td>&quot;</td>
<td>1 mM</td>
</tr>
<tr>
<td>C/C'4</td>
<td>&quot;</td>
<td>0.1 mM</td>
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</tbody>
</table>

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

Tools/materials needed: two-cuvette electrochemical cell, small clamps, two “fritted” aqueous Ag/AgCl (saturated with KCl) reference electrodes, pipe cleaners and/or paper clips, Parafilm, protonated Nafion membrane, scissors, hole punch, aqueous solutions of 100 mM salt (HCl, KOH, KCl, NaCl)
• Using your protonated Nafion membrane from part C, repeat the experiments in Part C, 2, ii only for the following aqueous concentrations of salt on each side of the Nafion membrane.

<table>
<thead>
<tr>
<th>Measurement #</th>
<th>Compartment #1</th>
<th>Compartment #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>100 mM HCl</td>
<td>100 mM KOH</td>
</tr>
<tr>
<td>D2</td>
<td>&quot;</td>
<td>100 mM KCl</td>
</tr>
<tr>
<td>D3</td>
<td>100 mM NaCl</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

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

Tools/materials needed: two-cuvette electrochemical cell, small clamps, two “fritted” aqueous Ag/AgCl (saturated with KCl) reference electrodes, pipe cleaners and/or paper clips, 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 C, 2, ii for the following aqueous concentrations of base on each side of the Nafion membrane.

<table>
<thead>
<tr>
<th>Measurement #</th>
<th>Compartment #1, KOH</th>
<th>Compartment #2, KOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>100 mM</td>
<td>100 mM</td>
</tr>
<tr>
<td>E2</td>
<td>&quot;</td>
<td>10 mM</td>
</tr>
<tr>
<td>E3</td>
<td>&quot;</td>
<td>1 mM</td>
</tr>
<tr>
<td>E4</td>
<td>&quot;</td>
<td>0.1 mM</td>
</tr>
</tbody>
</table>

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

Tools/materials needed: two-cuvette electrochemical cell, small clamps, two Ag/AgCl wires and two separate “fritted” tubes containing aqueous saturated KCl, pipe cleaners and/or paper clips, 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 C, 2, i and ii – in that order – for the following aqueous concentrations of acid on each side of the Sustainion membrane.

<table>
<thead>
<tr>
<th>Measurement #</th>
<th>Compartment #1, HCl</th>
<th>Compartment #2, HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>F/F1</td>
<td>100 mM</td>
<td>100 mM</td>
</tr>
<tr>
<td>F/F2</td>
<td>&quot;</td>
<td>10 mM</td>
</tr>
<tr>
<td>F/F3</td>
<td>&quot;</td>
<td>1 mM</td>
</tr>
<tr>
<td>F/F4</td>
<td>&quot;</td>
<td>0.1 mM</td>
</tr>
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</table>

Assignment (assigned with next week’s activity; due Tuesday, May 28, 2019 at the start of the lecture class); in the meantime, begin to analyze your data, because for the next assignment you will be required to interpret your data in the context of liquid-junction potentials, Donnan potentials, and related information that we discussed during the lecture classes.