CH302 Unit 8 Day 6 RAQ   Name:_____

Vanden Bout/LaBrake   UTEID:_____
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PART I. Lithium is used in two types of batteries, disposable lithium batteries and rechargeable lithium ion batteries. Lithium ion is found in the Earth's crust bound up in certain minerals and dissolved in the ocean and dissolved in the hot water that can be tapped into from geothermal jets.

1. Looking at the reduction potential table, state why one expects to find lithium in the natural world as an ion and not as a free metal

The battery industry employs metallic lithium as the anode material for a wide class of disposable batteries called, lithium batteries. These batteries are lightweight and have a much longer life than the cheaper zinc-copper cells. They are used in such varying applications as watches, pacemakers and remote lock car keys (fob). Due to the ever-expanding market for these batteries, there must be a well-accepted method of converting Li ion to Li metal.

Lithium is found at the bottom of the reduction table with the most negative value. It has the lowest reduction potential. This means that it is the easiest to oxidize. This also means that lithium is very reactive and ready to give up its electrons to become more stable. Therefore, when in contact with any of the other materials on the table it will always be spontaneously oxidized into the lithium ion.

2. One common method is to isolate the lithium ion in the form of a chloride salt from salt deposits near geothermal vents.   Given that you have isolated the salt, fully describe using a properly labeled sketch, how you would produce lithium metal from the salt   Include the type of electrochemical cell you would use to produce the lithium, complete with a description of the half reaction occurring at the anode, the cathode, the overall cell reaction, and the minimum potential necessary to run the cell.

The lithium chloride salt has a formula unit of: LiCl

We would need to set up an **electrolytic** cell. First, the LiCl would need to be **molten** in order for its ions to be mobile. I would melt solid LiCl and place to inert electrodes (platinum for example) into the molten solution. I would then apply a voltage across the electrodes. After running the cell, I would collect the solid Lithium at the bottom of my container.

Anode (Oxidation): $2Cl^-$ (l) $\rightarrow$ Cl_2 (g) + $2e^-$
Cathode (Reduction): Li^+ (l) + $1e^-$ $\rightarrow$ Li (s)
Overall: $2Cl^-$ + $2Li^+$ $\rightarrow$ 2Li (s) + Cl_2(g)
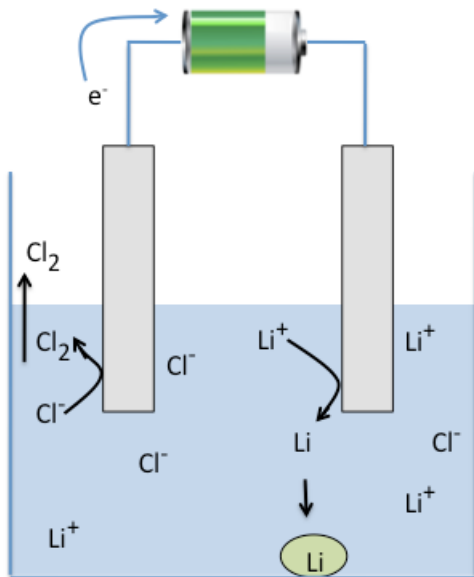
Minimum Potential Necessary:
The cell would have a negative potential (electrolytic):
$E° = E°_{cathode} - E°_{anode}$
$E° = (-3.05) – (1.36) = -4.41$ V
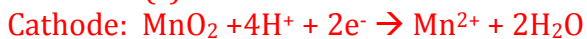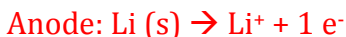So, we would have to apply a potential greater than 4.41V.

3. Calculate the amount of time it would take to produce 100 g of Li operating your cell at a current of 1 Amp.
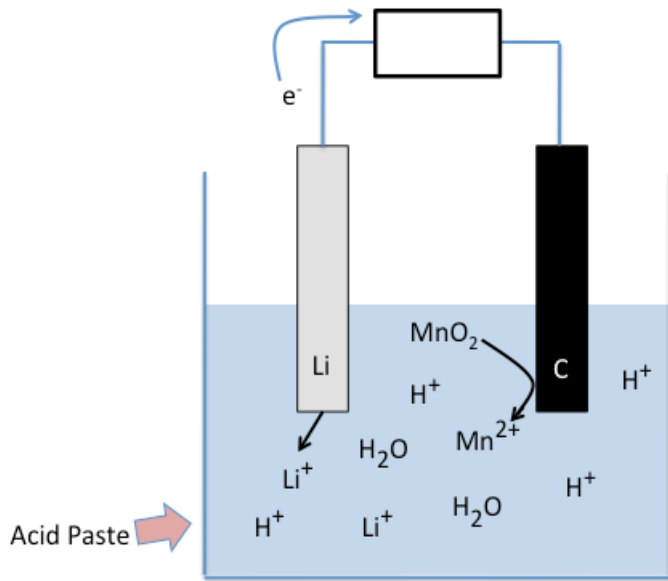
100 g Li	1 mol Li	2 mol e⁻	96485 C	1 second
	6.94 g Li	2 mol Li	1 mol e⁻	1 C

=1,390,273.78 seconds (23,171.2 minutes, 386.2 hours, 16.1 days, etc.)
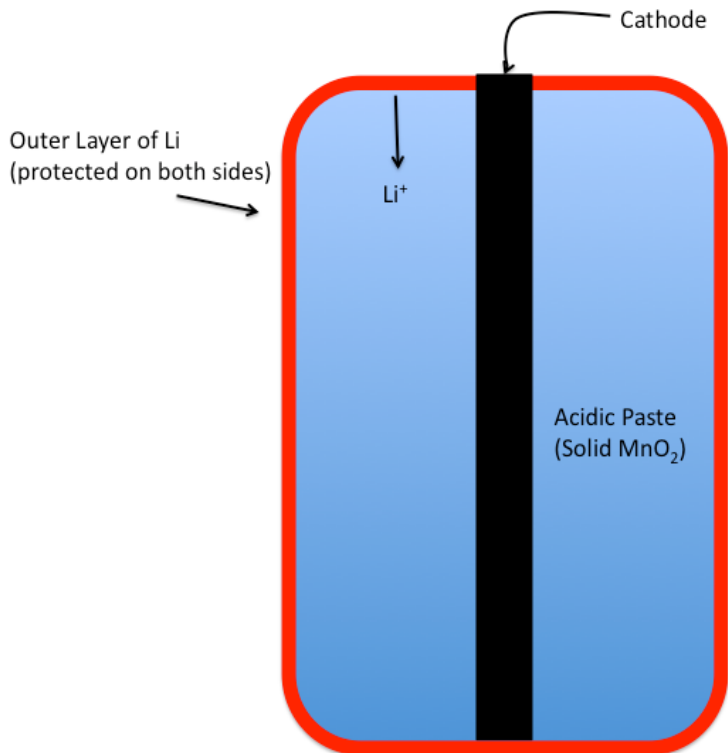
4. Please describe a voltaic cell that could be made using Li as the anode and MnO_2 in an acidic paste in the presence of a graphite cathode. Include in your description the balanced REDOX reaction.
We would need to set up to containers, connected by a salt bridge and an external wire. The anode cell would contain a solid Lithium electrode in a solution with lithium ions. The cathode cell would contain the graphite cathode coated with the solid MnO_2 and acidic paste in an acidic solution.

Anode: Li (s) → Li⁺ + 1 e⁻
Cathode: MnO_2 +4H⁺ + 2e⁻ → Mn^{2+} + $2H_2O$
Overall: 2Li +MnO_2 + 4H⁺ → 2Li⁺ + Mn^{2+} + $2H_2O$

OR

Cathode

Outer Layer of Li
(protected on both sides)

Li⁺

Acidic Paste
(Solid MnO_2)

5. State the standard cell potential of this cell.
$E° = E°_{cathode} - E°_{anode}$
$E° = 1.21 – (-3.05) = 4.26$ V

6. Calculate cell potential for a battery that has the following concentrations: Li ion is 0.4 M, the acid concentration is 0.1M and the Mn^{2+} concentration is 0.01 M.

$$E = E^O - \frac{0.0591}{n} \log Q$$

$$E = 4.26 - \frac{0.0591}{2} \log\left(\frac{(0.4)^2(0.01)}{(0.1)^4}\right)$$

$$E = 4.26 - \frac{0.0591}{2} \log(16)$$

$$E = 4.22$$

7. Calculate the free energy of the cell under standard conditions.
ΔG° = -nFE°
ΔG° = -(2)(96485)(4.26) = -822 kJ

PART II. A fuel cell is a device for converting chemical energy directly to electrical energy. Normally, when a fuel, such as hydrogen, natural gas (mostly methane), coal or petroleum, is "burned" heat energy is liberated. The heat is then used directly, for example for cooking or heating a home; or can be converted to mechanical energy via the expansion of a gas. The mechanical energy can then be converted to electrical energy in an electrical generator. In a fuel cell, the chemical energy is converted directly into electrical energy by separating the reactants and channeling the electrons through an external wire. Basically, the fuel is pumped into one half of the device, and the oxidizing agent is added to the other side.

The over all reaction for a hydrogen fuel cell is:

2H$_2$ + O$_2$ → H$_2$O
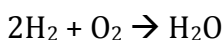
1. What serves as the fuel?   H$_2$

2. What serves as the oxidizing agent?
O$_2$ (since it is reduced)

This type of fuel cell allows protons to move across the membrane, but electrons are channeled around an external wire, such that their flow can be intercepted for doing electrical work. The diagram at the right shows part of a fuel cell. On one side hydrogen is being pumped in, on the other side oxygen is being pumped in. Protons cross a semi-permeable membrane, while the electrons move out an external wire and around to the other reactant.
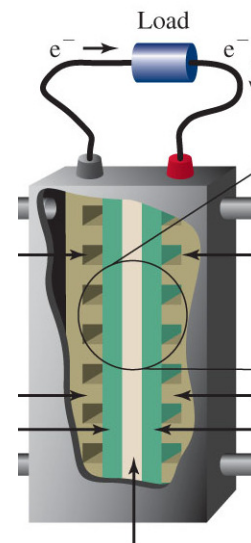
3. Please redraw the diagram showing where the hydrogen enters the cell, in what direction the protons flow, in what direction the electrons flow and where the oxygen enters the cell. Also label the anode and the cathode and predict whether or not you think those electrodes participate in the REDOX reaction. Label which side is undergoing oxidation and which side is undergoing reduction, and write the corresponding half reactions.

Electrodes are inert. The anode is the site at which hydrogen gas is oxidized into the hydrogen ion and the cathode is the site at which oxygen gas is reduced into the oxygen in a water molecule. Electrodes must be solid pieces of metal and hydrogen gas and oxgen gas are not solids! So the inert electrodes simply provided a means for the transfer of electrons to the reacting species.

Oxidation: $H_2 \rightarrow 2H^+ + 2e^-$ Reduction $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Overall: $2H_2 + O_2 \rightarrow 2H_2O$
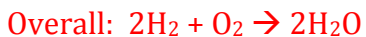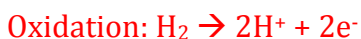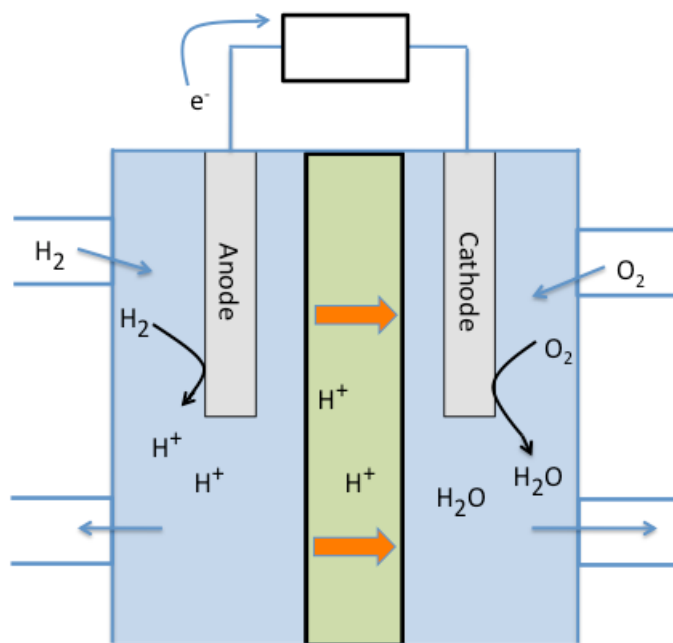
4. Assuming 100% efficiency how much electrical work can be done by a fuel cell supplied with 1 Kg of hydrogen and excess oxygen?

$E° = E°_{cathode} - E°_{anode}$
$E° = 1.23 – 0 = 1.23 V$

$-w = \Delta G° = -nFE°$
$\Delta G° = -(4)(96485)(1.23) = -474,706 J/mol rxn$
$-w = \Delta G°$
$w = 474,706 J/mol rxn$

1000g H_2	1 mol H_2	1 mol Rxn	474,706 J
	2 g H_2	2 mol H_2	1 mol Rxn

=1.18 x 10^8 J for 1 kg H_2
=1.18 x 10^5 kJ for 1 kg H_2

5. Calculate the value of the equilibrium constant for this cell reaction. Does the equilibrium lie to the reactant or product side? Would you expect the voltage to remain constant, to increase or to decrease as this fuel cell is running? Please explain your answer choice.

$$E = E^O - \frac{0.0591}{n}\log Q$$

$$0 = E^O - \frac{0.0591}{n}\log K$$

$$E^O = \frac{0.0591}{n}\log K$$

$$1.23 = \frac{0.0591}{4}\log K$$

$$K = 1.77 \times 10^{83}$$

Heavily on the products side! A large K means the products are favored!

As H_2 and O_2 are continuously being pumped into the system, so the voltage should remain constant. We are never changing the concentrations of the reactants because every time a little bit of these reactants are used up, we pump more into the system!

TABLE 11.1 Standard Reduction Potentials at 25°C (298 K) for Many Common Half-reactions

Half-reaction	$\mathscr{E}°$ (V)	Half-reaction	$\mathscr{E}°$ (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$IO_4^- + 2H^+ + 2e^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	-0.036
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	-0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	-0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	-0.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	-0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	-0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	-0.50
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	-0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	-0.83
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	-1.18
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	-1.66
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	-2.23
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	-2.37
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^- \rightarrow La$	-2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	-2.71
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^- \rightarrow Ca$	-2.76
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	-2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	-2.92
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	-3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		