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11 **Theory**

12 1. Theory on the open circuit cell potential

For sufficiently dilute solutions, the physical equilibrium for the dissolution of a gas into a liquid can be expressed by the Henry's law, which for the case of carbon dioxide, would be given by:

16
$$p_{\rm CO_2} = K_H \left[{\rm H}_2 {\rm CO}_3^* \right]$$
 (1)

17 where K_H is the Henry's coefficient and $[H_2CO_3^*]$ stands for the molar concentration, being 18 $H_2CO_3^*$ the sum of the dissolved $CO_2(aq)$ and the true carbonic acid H_2CO_3 . These two species 19 are conventionally lumped as they are difficult to distinguish.

- 20 The dissociation of H_2CO_3 in water is described by the stoichiometric equations:
- 21 $[H_2CO_3] \leftrightarrow [H^+] + [HCO_3^-]$ (2)
- 22 $\left[\mathrm{HCO}_{3}^{-}\right] \leftrightarrow \left[\mathrm{H}^{+}\right] + \left[\mathrm{CO}_{3}^{2-}\right]$ (3)
- 23 $[H_2O] \leftrightarrow [H^+] + [OH^-]$ (4)
- 24 and the corresponding equilibrium equations:

25
$$K_{a1} = \frac{\left[H^{+}\right]\left[HCO_{3}^{-}\right]}{\left[H_{2}CO_{3}^{*}\right]}$$
(5)

26
$$K_{a2} = \frac{\left[\mathrm{H}^{+} \right] \left[\mathrm{CO}_{3}^{2^{-}} \right]}{\left[\mathrm{HCO}_{3}^{-} \right]}$$
(6)

- 27 $K_w = \left[\mathrm{H}^+ \right] \left[\mathrm{OH}^- \right]$ (7)
- 28 The solution is electro-neutral, thus:

29
$$\left[\mathrm{H}^{+}\right] = \left[\mathrm{OH}^{-}\right] + \left[\mathrm{HCO}_{3}^{-}\right] + 2\left[\mathrm{CO}_{3}^{2-}\right]$$
 (8)

Given that the proton is the only cation, it implies that $[H^+] >> [OH^-]$ and that the pH will be acidic. We can thus safely assume that $[OH^-]$ and $[CO_3^{2-}]$ (given the high pK value of 10.3 of the second dissociation constant K_{a2}) can be neglected and, therefore, the electro-neutrality condition is simplified to:

$$34 \quad \left[\mathrm{H}^{+}\right] \approx \left[\mathrm{HCO}_{3}^{-}\right] \qquad (9)$$

35 We, therefore, can write from Eq. (5), using Eq. (9):

$$36 \quad \left[\mathrm{H}^{+} \right]^{2} = K_{a1} \left[\mathrm{H}_{2} \mathrm{CO}_{3}^{*} \right] \qquad (10)$$

- 37 and using Eq. (1)
- $38 \qquad \left[\mathbf{H}^{+}\right]^{2} = K_{a1} \cdot K_{H} \cdot p_{\mathrm{CO}_{2}} \qquad (11)$
- 39 which is equivalent to:

40
$$\left[\mathrm{H}^{+}\right] = +\sqrt{K_{a1} \cdot K_{H} \cdot p_{\mathrm{CO}_{2}}}$$
 (12)

41 The OCV of the cell is the sum of the anion and cation exchange membrane potentials.

42
$$E_{\text{OCV}} = E_{\text{mem, an}} + E_{\text{mem, cat}}$$
 (13)

43 or

44
$$E_{\text{OCV}} = \frac{RT}{F} \left(\ln \left(\frac{\left[H^+ \right]_h}{\left[H^+ \right]_l} \right) + \ln \left(\frac{\left[\text{HCO}_3^- \right]_h}{\left[\text{HCO}_3^- \right]_l} \right) \right)$$
(14)

45 Given Eq. (9) one can write:

46
$$E_{\text{OCV}} = \frac{RT}{F} 2 \ln \left(\frac{\left[H^+ \right]_h}{\left[H^+ \right]_l} \right) \quad (15)$$

47 And thus using Eq. (11) one can write

48
$$E_{\text{OCV}} = \frac{RT}{F} \ln\left(\frac{p_{\text{CO}_2,h}}{p_{\text{CO}_2,l}}\right) = \frac{RT}{F} \ln(\alpha)$$
(16)

which corresponds to the expression given for the theoretical upper limit for the cell potentialsystem in deionized water.

2. Relationship between partial pressure ratio and pH difference

From Eq. (15) and Eq. (16), we can write:

$$\ln\left(\alpha\right) = 2\ln\left(\frac{\left[\mathrm{H}^{+}\right]_{h}}{\left[\mathrm{H}^{+}\right]_{l}}\right)$$
(17)

Using Eq (11), we obtain:

$$\alpha = 10^{2(pH_l - pH_h)}$$
(18)

This relationship can be used to determine the partial pressure ratio from the pH difference between the solutions.

3. Theory on the maximal mixing energy

We will call the gas with the high CO₂ pressure the "high concentration gas", with pressure $p_{CO_2,h}$, and the gas with the low CO₂ level the "low concentration gas" with pressure $p_{CO_2,l}$. For an ideal gas, the chemical potential can be described as:

$$\mu_{\text{CO}_2,h} = \mu_{\text{CO}_2,h}^{\Theta} + RT \ln\left(\frac{p_{\text{CO}_2,h}}{p_{\text{CO}_2}^{\Theta}}\right)$$
(19)

where $\mu_{CO_2,h}$ is the chemical potential of the donor gas (J/mol), $\mu_{CO_2,h}^{\Theta}$ is the chemical potential under standard conditions and $p_{CO_2}^{\Theta}$ is the standard pressure of CO₂ used to define the standard chemical potential (Pa). In a similar way, this can be written for the low concentration gas. By lowering the partial pressure, the chemical potential goes down, and this decrease in chemical potential can potentially be harvested as work. The partial pressure can be lowered in a simple way by mixing with another gas mixture with a lower content of CO₂, such as air $(p_{CO_2} \sim 390 \text{ ppm})$. The partial pressure composition of the mixture depends on the amount of high- n_h (mol) and low-concentration gas n_l (mol) mixed.

$$p_{\text{CO}_{2,m}} = \frac{n_h p_{\text{CO}_{2,h}} + n_1 p_{\text{CO}_{2,l}}}{n_h + n_l}$$
(20)

The available work upon mixing W_{CO_2} equals the chemical energy in the high- and low concentration gases minus the chemical energy contained in the mixture, which can be written as:

$$W_{m} = n_{h} \frac{p_{\text{CO}_{2},h}}{p} \mu_{\text{CO}_{2},h} + n_{l} \frac{p_{\text{CO}_{2},l}}{p} \mu_{\text{CO}_{2},l} - \left(n_{h} \frac{p_{\text{CO}_{2},h}}{p} + n_{l} \frac{p_{\text{CO}_{2},l}}{p}\right) \mu_{m}$$
(21)

where p is the total pressure. This can be rewritten as the available work per mol of CO₂ present in the high concentration gas:

$$\frac{W_m}{n_h \frac{p_{\text{CO}_2,h}}{p}} = RT \left(ln \left(\frac{p_{\text{CO}_2,h}}{p_{\text{CO}_2,m}} \right) + \frac{n_l}{n_h} \frac{p_{\text{CO}_2,l}}{p_{\text{CO}_2,h}} ln \left(\frac{p_{\text{CO}_2,l}}{p_{\text{CO}_2,m}} \right) \right)$$
(22)

Using W_{CO_2} for the available work per mole of CO_2 in the high concentration gas,

$$\alpha = \frac{p_{\text{CO}_2,h}}{p_{\text{CO}_2,l}} \quad (23)$$

as the partial pressure ratio of high- relative to low-concentration gas, and

$$\beta = \frac{n_l}{n_h} \tag{24}$$

as the mixing ratio in quantities of gas, we get:

$$W_{\rm CO_2} = RT \left(\ln\left(\alpha\right) + \left(\frac{\beta}{\alpha} + 1\right) \ln\left(\frac{1+\beta}{\alpha+\beta}\right) \right)$$
(25)

With increasing β , more work can be extracted per amount of CO₂ in the high concentration gas. In the limit of an infinite amount of air, the following result can be obtained for the energy per mass of CO₂ in the high concentration gas,

$$W_{\rm CO_2,max} = \frac{RT}{M_{\rm CO_2}} \left(\ln(\alpha) + \frac{1}{\alpha} - 1 \right)$$
(26)

A temperature of 150 °C is representative of a situation where flue gas undergoes only limited gas treatment, while 50 °C is characteristic for a system with wet scrubbing. 20 °C is ambient temperature. Fig. S7 shows that the available work increases witch increasing partial pressure ratio and with increasing temperature. For the case of mixing of CO_2 emissions with infinite amount of air at 20 °C, up to 330 kJ per mol of CO_2 emitted can be harvested.





Fig. S1: (A) Schematic drawing of the setup. (B) Picture of the experimental setup used for this study.



Fig. S2. The capacitive cell. (**A**) Drawing of the cell and its different layers. (**B**) Picture of the cell open showing the two halves of the cell, Teflon gasket and polymer spacer on top at the left and Cation exchange membrane on top at the right. (**C**) Picture of the closed cell with a drawing of the flow pattern.



Fig. S3: Methodology followed to measure the OCV of the system when switching from one solution to another.



Fig. S4: Measured Cell potential and pH with decreasing P_{CO_2} in the CO₂ tank



Fig. S5. Thermodynamic cycle displayed in the accumulated charge (C) and Cell Potential plane (mV) Available work is given by the included surface of the thermodynamic cycle, for the process with deionized water (dashed blue line) and the process with the MEA solution (red solid line).



Fig. S6. OCV (mV) as function in response of alternating the air flushed and CO_2 flushed MEA solution.



Fig. S7. Available work per kg of CO_2 , as a function of the pressure ratio and the temperature