

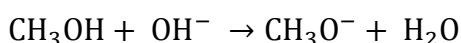
## Supplementary Information

### **Electrooxidation of methanol in an alkaline fuel cell:**

### **Determination of the nature of the initial adsorbate**

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#### **1. Calculation of equilibrium concentrations**



**Table S1:** Moles of each species present at equilibrium

Species	CH <sub>3</sub> OH	OH <sup>-</sup>	CH <sub>3</sub> O <sup>-</sup>	H <sub>2</sub> O
Initial conc. / M	0.05	0.05	0	55.56
Equilibrium conc. / M	0.05 - x	0.05 - x	x	55.56

Assume that small change in  $x$  does not affect molar concentration of water.

We can substitute the values in the final row of table S1 into the equilibrium expression derived in the paper, rearrange for  $x$  and solve using the quadratic equation:

$$K_{eq} = \frac{[\text{CH}_3\text{O}^-][\text{H}_2\text{O}]}{[\text{CH}_3\text{OH}][\text{OH}^-]} = 1.58 = \frac{55.56x}{(0.05 - x)^2}$$

$$1.58 = \frac{55.56x}{x^2 - 0.1x + 2.5 \times 10^{-3}}$$

$$1.58x^2 - 0.158x + 3.95 \times 10^{-3} = 55.56x$$

$$1.58x^2 - 55.718x + 3.95 \times 10^{-3} = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \text{ where } a = 1.58, b = -55.718 \text{ and } c = 3.95 \times 10^{-3}$$

$$x = 32.26 \text{ and } 7.09 \times 10^{-5}$$

Taking the only meaningful value of  $x$  in this context yields the concentration of each species at equilibrium (see Table 1 in main text).

## 2. Estimation of effective energy difference between methanol and methoxide, in solution, at 353 K

$$\frac{[CH_3O^-]}{[CH_3OH]} = e^{-\frac{\Delta E}{RT}} = \frac{7.089 \times 10^{-5}}{0.04993} = 1.41979 \times 10^{-3}$$

$$\Delta E = -RT \ln(1.41979 \times 10^{-3}) = -8.314472 * 353.15 * \ln(1.41979 \times 10^{-3})$$

$$\Delta E = 19253.76 \text{ Jmol}^{-1}$$

$$\Delta E = 0.20 \text{ eV}$$

### 3. Cluster-continuum model Calculations

The change in solvation entropy for methanol and methoxide was obtained according to the following (expressed in terms of methoxide):

Let  $S(CH_3O^-)_{(g)}$  be the entropy of the methoxide ion in the gas phase as obtained from Gaussian.

Let  $S(H_2O)_n(aq)$  represent the entropy of a cluster of  $n$  explicit water molecules in the aqueous phase, and let  $S(CH_3O^-)(H_2O)_n(aq)$  represent the entropy of the methoxide ion surrounded by a cluster of  $n$  explicit water molecules, in the aqueous phase.

For each of these clusters the aqueous phase entropy can be expressed as the sum of the entropy of the corresponding gas phase cluster and the shift in entropy due to the bulk solvent as shown in equations 1 and 2.

$$S(H_2O)_n(aq) = S(H_2O)_n(g) + \Delta S_{solv}[(H_2O)_n] \quad (1)$$

$$S(CH_3O^-)(H_2O)_n(aq) = S(CH_3O^-)(H_2O)_n(g) + \Delta S_{solv}[(CH_3O^-)(H_2O)_n] \quad (2)$$

The gas phase entropy component of equations 1 and 2 is obtained from the optimised structure in Gaussian. The change in entropy of solvation,  $\Delta S_{solv}$ , for the gas phase cluster of  $n$  explicit water molecules in the case of equation 1 ( $n$  explicit water molecules surrounding the methoxide ion in the case of equation 2) being solvated in the bulk solvent, is also obtained using Gaussian, with the implementation of the PCM solvation model.

Finally, equation 3 represents the entropy change of solvation of the methoxide ion

$$\Delta S_{solv}[CH_3O^-, n] = \Delta S_{gas}[CH_3O^-, n] + \Delta \Delta S_{solv}[CH_3O^-, n] \quad (3)$$

$$\text{where } \Delta S_{gas}[CH_3O^-, n] = S(CH_3O^-)(H_2O)_n(g) - S(H_2O)_n(g) - S(CH_3O^-)_{(g)} \quad (4)$$

$$\Delta \Delta S_{solv}[CH_3O^-, n] = \Delta S_{solv}[(CH_3O^-)(H_2O)_n] - \Delta S_{solv}[(H_2O)_n] \quad (5)$$

Equation 4 represents the contribution that the explicit water molecules make to the entropy change of solvation of methoxide; the number,  $n$ , of explicit water molecules in the below examples is three. Equation 5 represents the effects due to the bulk (PCM) solvent.

Using the Gaussian results in the Table S2 (below) we can estimate the barriers to the adsorption of methanol and methoxide.

**Table S2:** Gaussian Entropy results for estimation of adsorption barriers.

	Gas phase S / Cal mol <sup>-1</sup> K <sup>-1</sup>	IEFPCM S / Cal mol <sup>-1</sup> K <sup>-1</sup>
CH <sub>3</sub> OH	56.964	56.993
CH <sub>3</sub> O <sup>-</sup>	52.747	55.000
CH <sub>3</sub> OH_3H <sub>2</sub> O	102.063	103.319
CH <sub>3</sub> O <sup>-</sup> _3H <sub>2</sub> O	112.343	113.398
3H <sub>2</sub> O	79.067	85.642

#### 4. Calculation of the TS<sub>soln</sub> barrier for methanol

$$\Delta S_{solv}[CH_3OH, n] = \Delta S_{gas}[CH_3OH, n] + \Delta \Delta S_{solv}[CH_3OH, n] \quad (\text{Equation 3})$$

$$\text{Let } \Delta S_{gas}[CH_3OH, n] = X = S[(CH_3OH)(H_2O)_{3(g)}] - S[(H_2O)_{3(g)}] - S[(CH_3OH)_{(g)}] \quad (\text{Equation 4})$$

$$X = 102.063 - 79.067 - 56.964 = -33.968 (\text{Cal mol}^{-1} \text{K}^{-1})$$

$$\text{Let } \Delta \Delta S_{solv}[CH_3OH, n] = Y = \Delta S_{solv}[(CH_3OH)(H_2O)_3] - \Delta S_{solv}[(H_2O)_3] \quad (\text{Equation 5})$$

$$Y = (103.319 - 102.063) - (85.642 - 79.067) = -5.319 (\text{Cal mol}^{-1} \text{K}^{-1})$$

$$\Delta S_{solv}[CH_3OH, n] = X + Y = -33.968 + -5.319 = -39.287 (\text{Cal mol}^{-1} \text{K}^{-1}) = -1.705 \times 10^{-3} (\text{eV K}^{-1})$$

For the reaction  $CH_3OH_{(g)} \rightarrow CH_3OH_{(aq)}$

$$\Delta S_{solv} = S_{soln} - S_g$$

$$\therefore S_{soln} = \Delta S_{solv} + S_g$$

$$S_g = 239.81 \text{ JK}^{-1} \text{ mol}^{-1} \text{ (from reference 1)}$$

$$S_g = 2.486 \times 10^{-3} \text{ eVK}^{-1}$$

$$\therefore S_{soln} = \Delta S_{solv} + S_g = -1.705 \times 10^{-3} + 2.486 \times 10^{-3} = 7.807 \times 10^{-4} \text{ eVK}^{-1}$$

$$TS_{soln} = 0.28 \text{ eV at } 353.15 \text{ K}$$

## 5. Calculation of the $TS_{soln}$ barrier for methoxide

$$\Delta S_{solv}[CH_3O^-, n] = \Delta S_{gas}[CH_3O^-, n] + \Delta \Delta S_{solv}[CH_3O^-, n] \quad (\text{Equation 3})$$

$$\text{Let } \Delta S_{gas}[CH_3O^-, n] = X = S[(CH_3O^-)(H_2O)_{3(g)}] - S[(H_2O)_{3(g)}] - S[(CH_3O^-)_{(g)}] \quad (\text{Equation 4})$$

$$X = 112.343 - 79.067 - 52.747 = -19.471 \text{ Cal mol}^{-1} \text{ K}^{-1}$$

$$\text{Let } \Delta \Delta S_{solv}[CH_3O^-, n] = Y = \Delta S_{solv}[(CH_3O^-)(H_2O)_3] - \Delta S_{solv}[(H_2O)_3] \quad (\text{Equation 5})$$

$$Y = (113.398 - 112.343) - (85.642 - 79.067) = -5.520 \text{ Cal mol}^{-1} \text{ K}^{-1}$$

$$\Delta S_{solv}[CH_3O^-, n] = X + Y = -19.471 + -5.52 = -24.991 \text{ Cal mol}^{-1} \text{ K}^{-1} = -1.084 \times 10^{-3} \text{ eV K}^{-1}$$

For the reaction  $CH_3O^-_{(g)} \rightarrow CH_3O^-_{(aq)}$

$$\Delta S_{solv} = S_{soln} - S_g$$

$$\therefore S_{soln} = \Delta S_{solv} + S_g$$

$$S_g = 52.747 \text{ Cal mol}^{-1} \text{ K}^{-1} \text{ (from Gaussian - see table above)}$$

$$S_g = 2.289 \times 10^{-3} \text{ eV K}^{-1}$$

$$S_{soln} = \Delta S_{solv} + S_g = -1.084 \times 10^{-3} + 2.289 \times 10^{-3} = 1.205 \times 10^{-3} \text{ eV K}^{-1}$$

$$TS_{soln} = 0.43 \text{ eV at } 353.15 \text{ K}$$

## Reference

1. P. Atkins and J. de Paula, *Atkin's Physical Chemistry 8th edition*; **2006**.