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成果報告 6

Methanol Decomposition Pathway through Electro-oxidation by Platinum

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1. Introduction

Direct methanol fuel cell (DMFC), whose name is derived from the employment of methanol as fuel, is getting more attention due to some advantages it has over its counterparts as follows: (1) it occupies lesser volumes compared to hydrogen powered FC's; (2) it has lesser potential hazards than that of pressurized hydrogen; (3) as a carbonaceous fuel reformers are not necessary and consequently, (4) lower weight requirements make it ideal for use in portable devices. However, there are some major drawbacks that need to be given attention. Since the fuel cell has to be operated at low temperatures, large platinum loadings are required but usage of pure platinum in the anode means higher capital costs thus, making any type of fuel cell is commercially non-feasible. Methanol cross-over from the anode to the cathode is also a major concern in DMFC's since it causes low fuel utilization as the air at the cathode combusts the permeated fuel leading to low power outputs. It is desired that another metal catalyst that can be integrated with platinum be found without jeopardizing the maximum power output (Gogel et al (1)). Ruthenium is commonly used but fuel cell costs remain high.

2. Gaussian 03 Calculations

In this study, the first significant step that can be taken is the elucidation of the platinum-methanol reaction mechanisms proposed by Hamnett (2). The equations are as follows:

$$CH_3OH + Pt_{(s)} \rightarrow Pt\text{-}CH_2\text{-}OH + H^+ + e^-$$

$$Pt\text{-}CH_2\text{-}OH + Pt_{(s)} \rightarrow Pt_2CHOH + H^+ + e^-$$

$$Pt_2CHOH + Pt_{(s)} \rightarrow Pt_3COH + H^+ + e^-$$

$$Pt_3COH \rightarrow Pt\text{-}CO + 2Pt_{(s)} + H^+ + e^-$$

$$Pt(s) + H_2O \rightarrow Pt\text{-}OH + H^+ + e^-$$

$$Pt\text{-}OH + Pt\text{-}CO \rightarrow Pt\text{-}COOH$$

or, in place of the last 2 steps:

$$Pt\text{-}CO + H_2O \rightarrow PtCOOH + H^+ + e^-$$

$$PtCOOH \rightarrow Pt_{(s)} + CO_2 + H^+ + e^-$$

Gaussian 03 calculations are performed to calculate the energies and optimize structures of the products and intermediates. Results obtained from previous calculations using Hartree-Fock theory (HF), i.e. before the summer campaign, were used as input parameters using density functional theory. Results using this theory are tabulated below:

	Species bonded to Pt	SCF energy (eV)	bond length with Pt (Å)
1	CH_2OH	-8.61	2.00
2	CHOH	-12.96	2.01
3	CHO	-17.32	1.99
4	CO	-8.54	1.79
5	OH	-7.16	1.90
6	COOH	-11.33	1.93

Table 1: DFT theory calculation results

3. Calculation Time and CPU usage

For a maximum memory usage of 6.29 MB and 0.4 CPU, the longest successful calculation was about 54.5 min and shortest was 57.5 sec. Calculation speeds are impressive and about 3 to 4 times faster than a 4 GB-memory 2.8 GHz alpha-2 workstation.

4. Ongoing Calculations

Present calculations are focused on transition structures, however this is rather difficult and may take much more time than ordinary optimizations.

References:

1. Gogel, V., Frey, T., Yongsheng, Z., Friedrich, K.A., Jörissen, L., Garche, J., Performance and methanol permeation of direct methanol fuel cells: dependence on operating conditions and on electrode structure, Journal of Power Sources 127 (2004) 172-180Hamnett, A.,. Mechanism and electrocatalysis in the direct methanol fuel cell, Catalysis Today 38 (1997), 445-457Foresman, J., Frisch, Æ., Exploring Chemistry with Electronic Structure Methods 2nd ed, 1995-96