Supporting Information

Bio-butanol as Fuel for Direct Alcohol Fuel Cells - Investigation of Sn Modified Pt Catalyst for Butanol Electro-oxidation

Vinod Kumar Puthiyapura, †,⊥ Dan J L Brett, ‡ Andrea E Russell, § Wen-Feng Lin,*†,‼ and Christopher Hardacre*†,⊥

†Centre for the Theory and Application of Catalysis (CenTACat), School of Chemistry and Chemical Engineering, Queen’s University of Belfast (QUB), Belfast, BT9 5AG, UK.

⊥School of Chemical Engineering and Analytical Science, The University of Manchester, The Mill, Manchester, M13 9PL, UK.

‼Department of Chemical Engineering, Loughborough University, Loughborough, Leicestershire, LE11 3TU, UK.

‡Department of Chemical Engineering, University College London (UCL), London WC1E 7JE, UK.

§Department of Chemistry, University of Southampton, High Field, Southampton, SO17 1BJ, UK.

Corresponding Authors

*Email: w.lin@lboro.ac.uk (W.L).

*Email: c.hardacre@manchester.ac.uk (C.H.).
In-situ FTIR analysis

The in-situ FTIR analysis was carried out with Cary 670 FTIR (Agilent Technologies) equipped with liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector. A homemade three electrode cell with a flat CaF$_2$ window was used for the electrochemical analysis as given in schematic in Figure S1. The working electrode was a glassy carbon electrode with diameter of 7 mm. A Ag/AgCl-3M NaCl and Pt wire were used as reference and counter electrode, respectively. The electrolyte was purged with N$_2$ before the experiments and also the flow was kept on the top of the solution during the experiments. A few interferogram was collected at a reference potential $R(E_1)$ and after the potential is switched to $E_2$ and a series of $R(E_2)$ were collected at same number of interferogram as $R(E_1)$. The resultant FTIR spectrum was calculated according to the equation below,

$$\frac{\Delta R}{R} = \frac{R(E_2) - R(E_1)}{R(E_1)}$$

In general, the negative going band denotes the formation of intermediate or product species and the positive going band indicate the consumption of a reactant or other species.

Figure S1. Schematic representation of the in-situ FTIR cell set up.
Figure S2. *In-situ* FTIR spectra of n-Butanol oxidation on Pt in 0.1M n-BtOH+0.1M H₂SO₄ solution. E₁ = -0.20 V, E₂ varied from -0.20 V to 1.20 V with an increment of 100 mV. Resolution 16 cm⁻¹, Numbers of scan 100.
Figure S3. The CV of Pt in 0.1 M 2-BtOH+0.1 M H$_2$SO$_4$ solution with different anodic potential limits. The cathodic potential was fixed to -0.22 V. The current was normalized by the A$_r$ of Pt. GC area = 0.3846 cm$^2$.

Figure S4. In-situ FTIR spectra of 2-Butanol oxidation on Pt in 0.1M 2-BtOH+0.1M H$_2$SO$_4$ solution. E$_1$=-0.20 V, E$_2$ varied from -0.20 V to 1.20 V with an increment of 100 mV. Resolution: 4 cm$^{-1}$; Numbers of scan = 32.
Figure S5. The CV of Pt and PtSn electrode in 0.1M H$_2$SO$_4$. Scan rate 50 mVs$^{-1}$. The difference in the $A_r$ of Pt and PtSn were used to calculate the tin coverage on Pt.

Figure S6. Voltammogram of PtSn(3:1) alloy catalyst in 0.5M $n$-BtOH+0.1M HClO$_4$ at room temperature. The voltammogram of Pt/C(40%) commercial catalyst in the same electrolyte is also given.
Figure S7. The Arrhenius plots of n-Butanol oxidation on Pt/C (40%) commercial catalyst in 0.5M n-BtOH+0.1M HClO₄ at three different potentials (0.62 V, 0.70 V and 1.1 V).

Figure S8. The Arrhenius plot of n-Butanol oxidation on PtSn (3:1)/C catalyst in 0.5M n-BtOH+0.1M HClO₄ at different potentials.
Figure S9. The PGPS voltammogram of PtSn (3:1) catalyst in x M n-BtOH+0.1M HClO₄. Scan rate 50 mVs⁻¹. Current normalized by the Aᵣ in 0.1M HClO₄.