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(E1) 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.

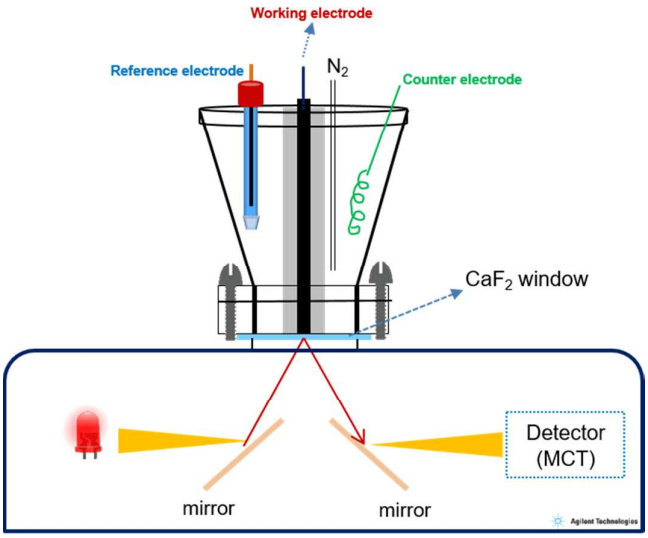

Figure S1. Schematic representation of the in-situ FTIR cell set up.

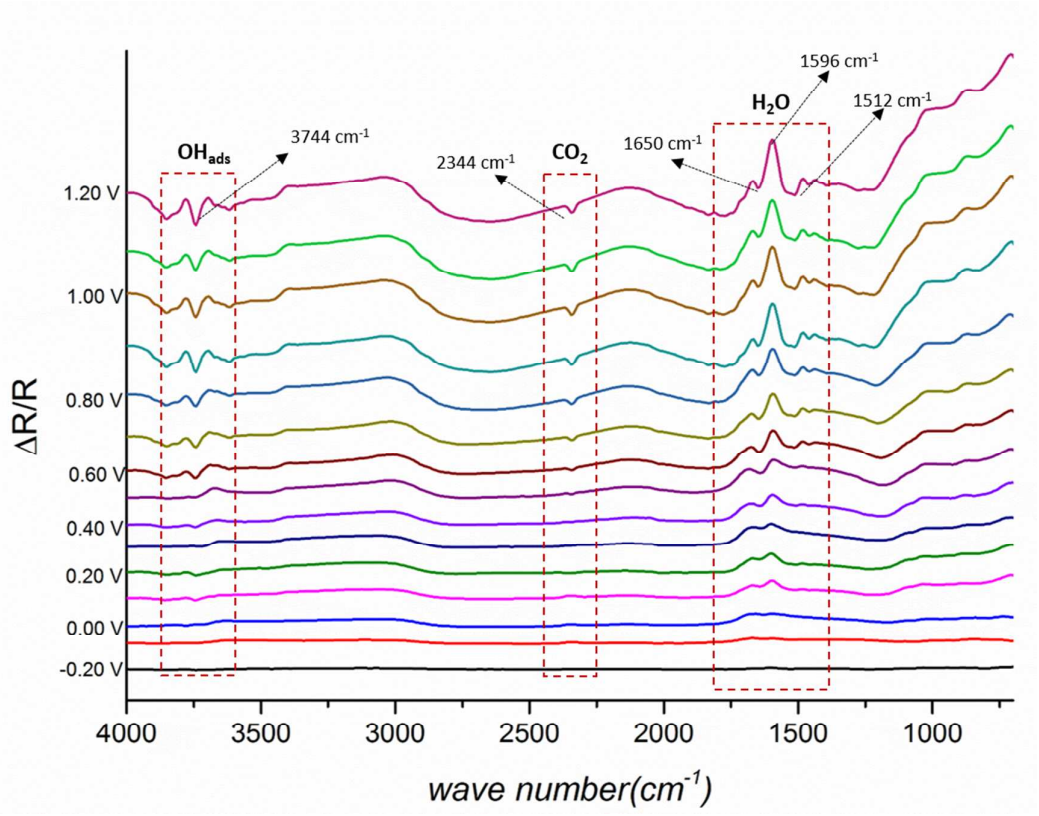

Figure S2. *In-situ* FTIR spectra of n-Butanol oxidation on Pt in 0.1M n-BtOH+0.1M H_2SO_4 solution. E_1= -0.20 V, E_2 varied from -0.20 V to 1.20 V with an increment of 100 mV. Resolution 16 cm^{-1}, Numbers of scan 100.

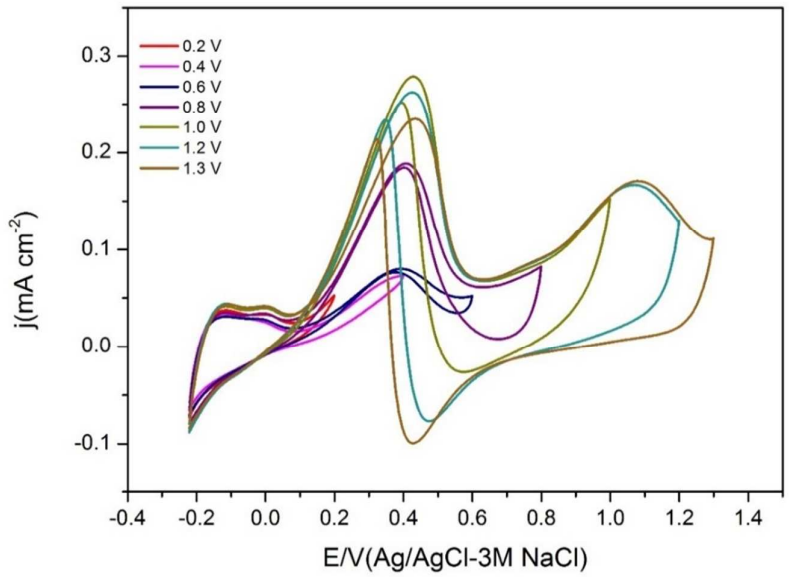

Figure S3. The CV of Pt in 0.1 M 2-BtOH+0.1 M H_2SO_4 solution with different anodic potential limits. The cathodic potential was fixed to -0.22 V. The current was normalized by the A_r of Pt. GC area = 0.3846 cm^2.

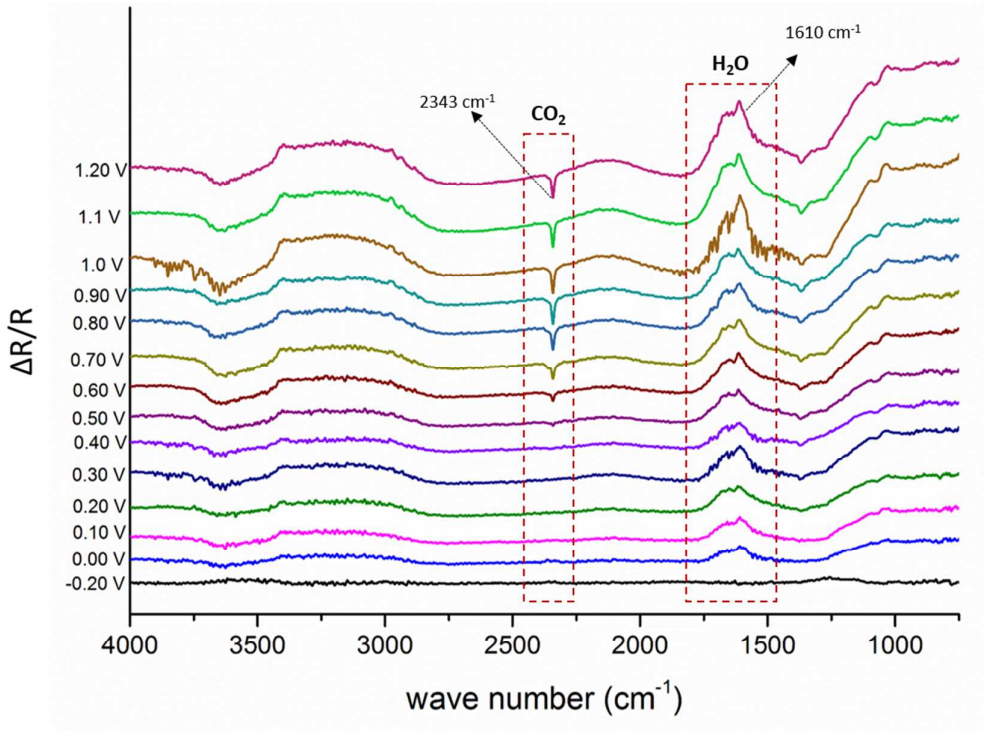

Figure S4. *In-situ* FTIR spectra of 2-Butanol oxidation on Pt in 0.1M 2-BtOH+0.1M H_2SO_4 solution. E_1=-0.20 V, E_2 varied from -0.20 V to 1.20 V with an increment of 100 mV. Resolution: 4 cm^{-1}; Numbers of scan = 32.

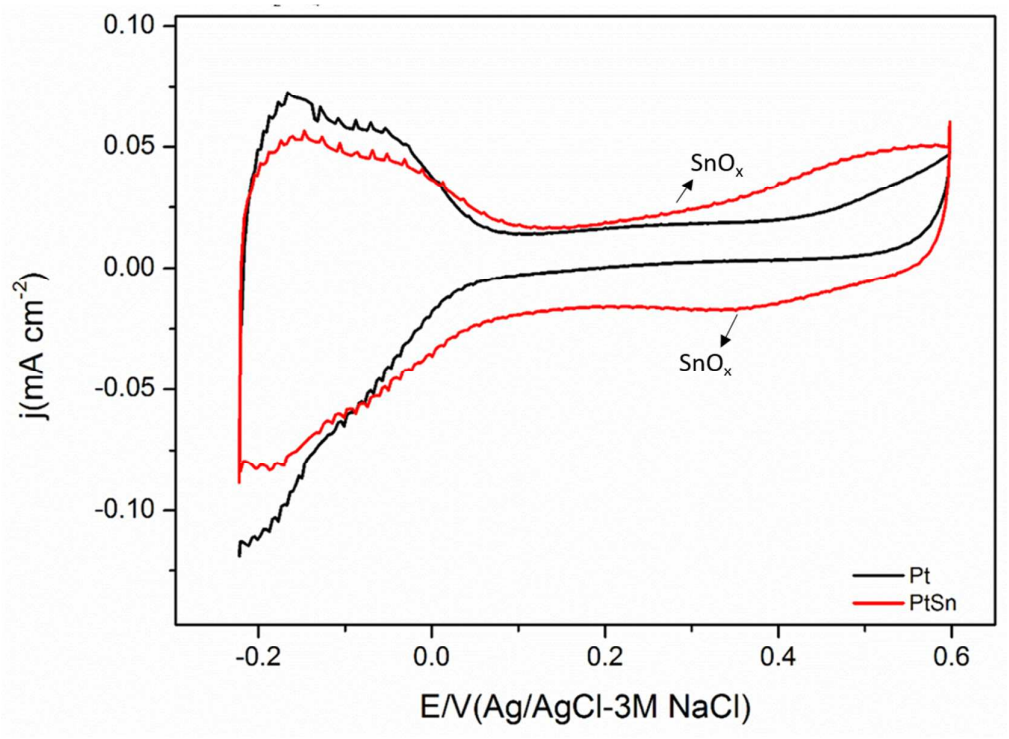

Figure S5. The CV of Pt and PtSn electrode in 0.1M H_2SO_4. Scan rate 50 mVs^{-1}. The difference in the A_r of Pt and PtSn were used to calculate the tin coverage on Pt.

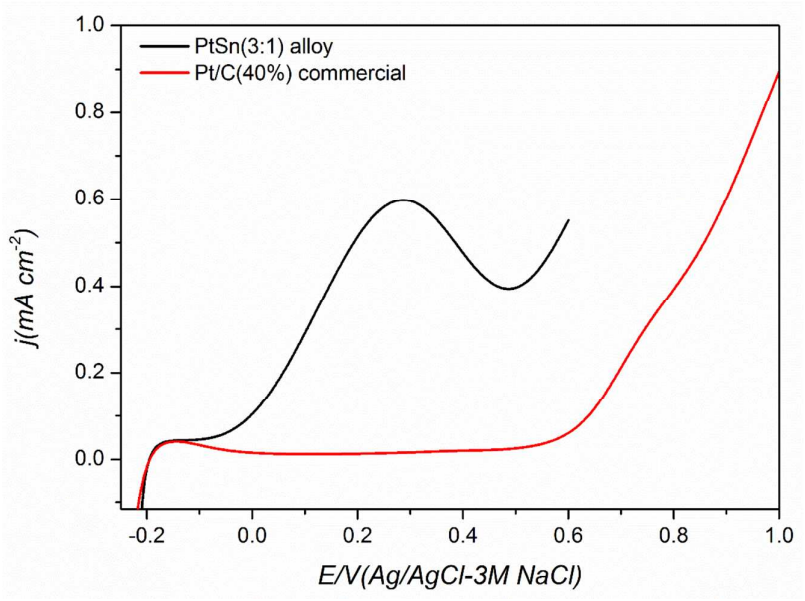

Figure S6. Voltammogram of PtSn(3:1) alloy catalyst in 0.5M *n*-BtOH+0.1M $HClO_4$ at room temperature. The voltammogram of Pt/C(40%) commercial catalyst in the same electrolyte is also given.

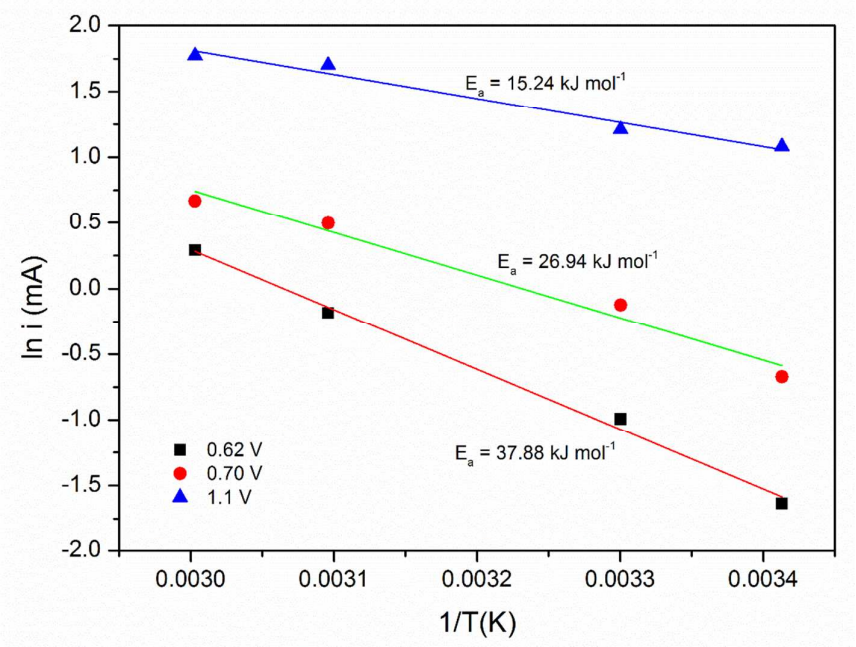

Figure S7. The Arrhenius plots of n-Butanol oxidation on Pt/C(40%) commercial catalyst in 0.5M *n*-BtOH+0.1M $HClO_4$ at three different potentials (0.62 V, 0.70 V and 1.1 V).

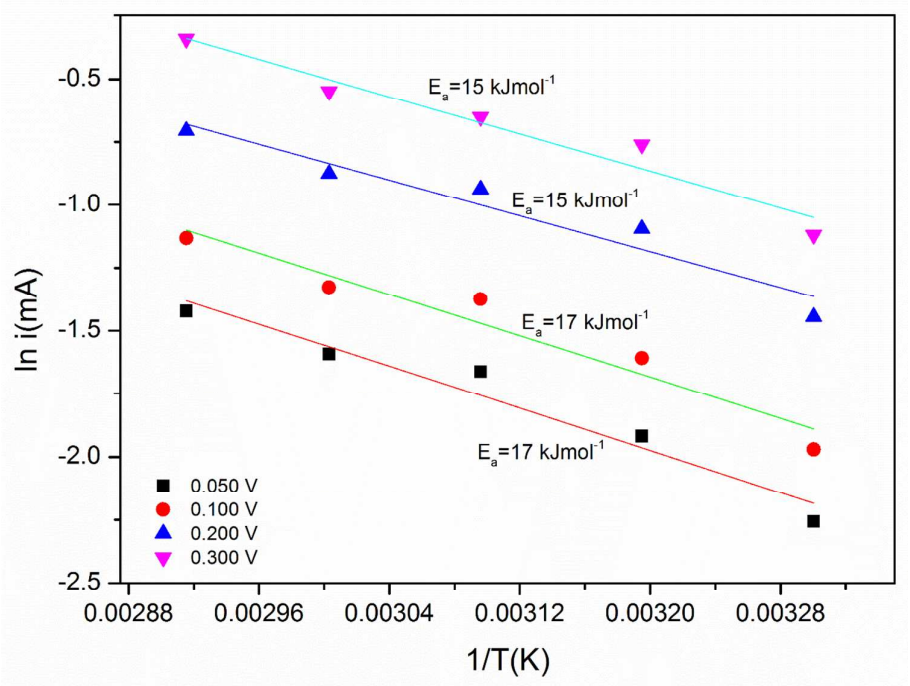

Figure S8. The Arrhenius plot of n-Butanol oxidation on PtSn (3:1)/C catalyst in 0.5M *n*-BtOH+0.1M $HClO_4$ at different potentials.

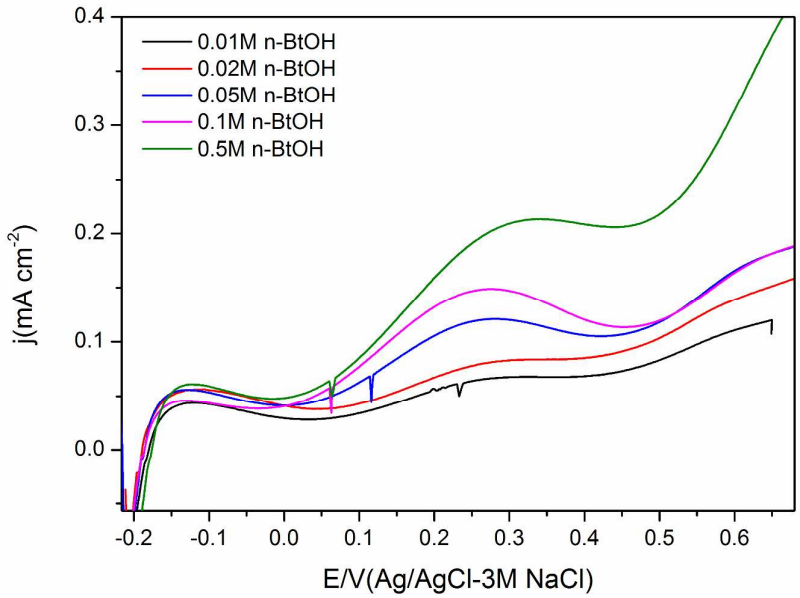

Figure S9. The PGPS voltammogram of PtSn (3:1) catalyst in x M n-BtOH+0.1M $HClO_4$. Scan rate 50 mVs^{-1}. Current normalized by the A_r in 0.1M $HClO_4$.