

## **Electronic Supporting Information**

### **Origin of the Cathodic Current Peak in the Cyclic Voltammetry of Methanol Electro-oxidation on Pt-based Electrocatalysts: A Revisit to the Goodenough Criterion**

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## **MATERIALS AND METHODS**

### *I. Electro-catalysts*

The two commercial catalysts were carbon-supported Pt at 40wt% loading (Pt/C) and carbon-supported Pt:Ru at 40:20wt% loading (PtRu/C), which were available courtesy of Johnson-Matthey. The catalysts were used as-received with further modification, unless noted in the experimental procedure for Pt activation via electrochemical cycling. The samples were imaged by a JEOL-2100 LaB<sub>6</sub> on copper grids. The as-received commercial Pt/C and PtRu/C electro-catalysts provided by J-M are displayed in Figure S1A and S1B, respectively. The TEM images show that the metal NPs on the carbon support are similarly sized between 4-6nm, therefore, this parameter along with synthesis should not be a contributing factor in this study.

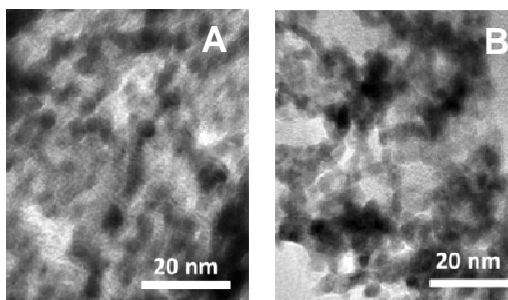


Figure S1: TEM images of Pt/C (A) and PtRu/C (B).

### *II. Electrochemical Measurements*

The electrochemical measurements were performed in an Ar-blanketed conventional three electrode electrochemical cell using a CHI 760c potentiostat (CHI Instrument, Inc) that was controlled by a computer with CHI software. The

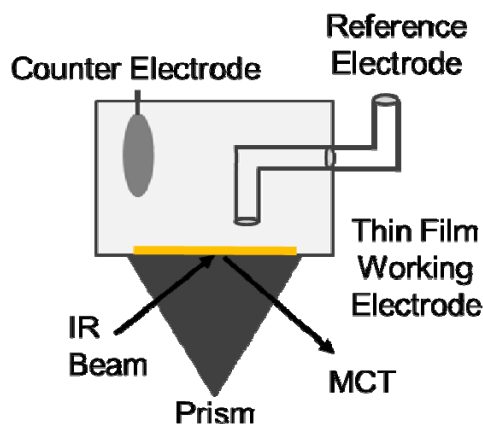
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° Contributed equally to this work

electrochemical experiments were recorded with a 50mV/s scan rate, unless specifically noted. The electrode potentials reference the Ag/AgCl (3M) electrode (0.265V with respect to RHE in 0.1M HClO<sub>4</sub>). The currents reported are normalized with respect to the Pt surface area, which is determined by the hydrogen desorption charge per area, 220 $\mu$ C/cm<sup>2</sup>.<sup>1</sup> Commercial Ag/AgCl (3M; CH Instrument, Inc) and Pt gauze electrodes were the reference and counter electrodes, respectively. The working electrode, comprised of a well-polished 3mm commercial glassy carbon electrode (GCE) (BioAnalytical Systems, Inc), had catalysts deposited onto it. The catalyst deposition involved a dilute suspension of NPs in ethanol that was drop cast onto the GCE and allowed to air dry. The supporting electrolyte solution was 0.1M HClO<sub>4</sub> that was prepared with milli-Q water (18.2M $\Omega$ ). Carbon monoxide (CO) oxidations were performed by adsorbing ultra-high purity CO gas, with the potential held at 0.1V, to the NP surface via 5min of purging the electrolyte, subsequently 15min of Ar purging to remove excess CO from the supporting electrolyte. Methanol oxidation was carried out in 0.1M HClO<sub>4</sub> + 0.5M CH<sub>3</sub>OH and again, the potential was held at 0.1V for 300s before electrochemical measurement.

### III. ATR-SEIRAS Measurements

The SEIRAS measurements were collected on a Bruker Vector-22 Infrared Spectrometer equipped with a liquid-nitrogen-cooled mercury-cadmium-telluride (MCT) detector that was modified to house an EC-IR cell and an optical reflection accessory with an incident angle of >60° for total attenuation reflection (Scheme S1). The obtained spectra are shown in the absorbance units defined as  $-\log(I/I_0)$  where  $I$  and  $I_0$  are the single-beam spectral intensities at the measuring potential and the reference potential, respectively. The upward/downward peak reveals the increasing/decreasing for the amount of the adsorbed species as compared to those at the reference spectrum. The spectrum was collected during a potential step experiment with a 0.1V step size and 200 scans taken at each step with 4 cm<sup>-1</sup> spectral resolution.



Scheme S1: A schematic of the ATR-SEIRAS apparatus.

The in-situ electrochemical measurements were performed in an N<sub>2</sub>-purged three electrode electrochemical cell using an EG&G 273A potentiostat (Princeton Applied Research) that was controlled by a computer with CoreWare software (Scribner). Commercial Ag/AgCl (3M) (CH Instrument, Inc) and Pt gauze electrodes were again used as the reference and counter electrodes, respectively. The working electrode was

comprised of a well-polished triangular Si prism that had a thin Au film chemically deposited onto the surface.<sup>2</sup> The catalysts were deposited directly onto the Au film as an aqueous 100 $\mu$ L droplet and then allowed to air dry. For each catalyst, the aqueous slurry was made with 100 $\mu$ g of Pt per 100 $\mu$ L of milli-Q water. The catalysts on the Au film were monitored between IR scan-potential step experiments via CV between -0.25 and 0.6V in order to ensure that the system was stable using similar procedures as in the electrochemical experiments. The CV spectra were performed in 0.1M HClO<sub>4</sub> with the stair measurements conducted in the potential range of -0.25 $\rightarrow$ 1.1 $\rightarrow$ -0.2V for Pt/C and -0.25 $\rightarrow$ 0.7 $\rightarrow$ -0.2V for the PtRu/C samples. The methanol oxidation was performed in 0.1M HClO<sub>4</sub> + 0.5M CH<sub>3</sub>OH in the range of -0.25 $\rightarrow$ 1.1 $\rightarrow$ -0.2V.

## RESULTS

### I. *In situ* ATR-SEIRAS Spectra

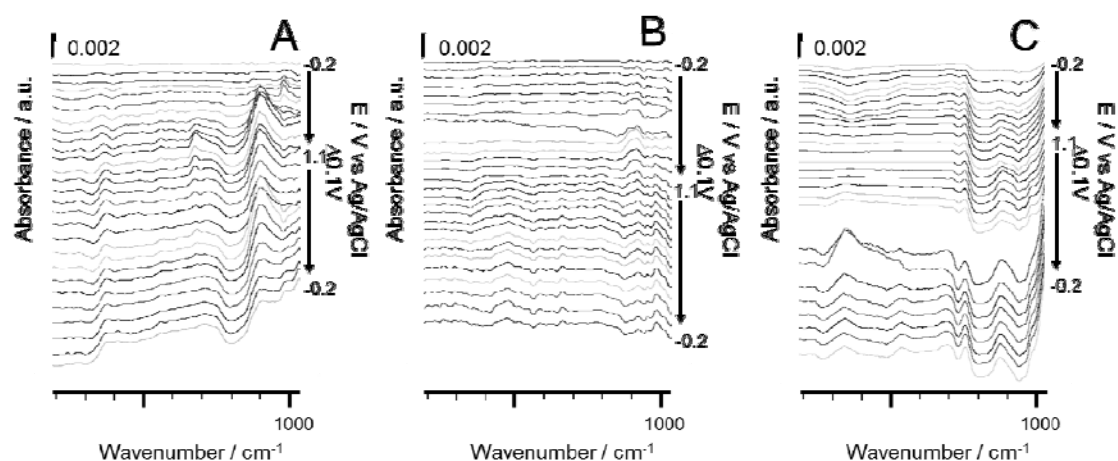


Figure S2: Potential difference spectra as a function of potential on Pt/C (A), unactivated (B) and activated PtRu/C (C). Scanning top to middle to bottom, -0.2 to 1.1 to -0.2V with  $\Delta 0.1$ V and reference at -0.25V of the positive (anodic) sweep.

### II. *In situ* ATR-SEIRAS of Adsorbed CO

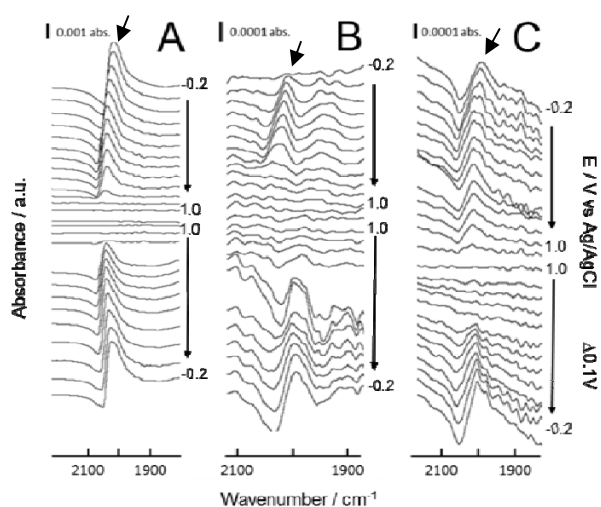


Figure S3: Potential difference spectra of adsorbed CO as a function of potential on Pt/C (A), unactivated (B) and activated PtRu/C (C). Scanning top to middle to bottom, -0.2 to 1.1 to -0.2V with  $\Delta 0.1V$  and reference at 1.1V.

### III. In situ ATR-SEIRAS of Adsorbed MeOH

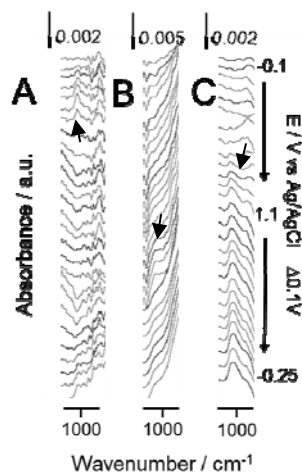


Figure S4: Potential difference spectra of adsorbed MeOH as a function of potential on Pt/C (A), unactivated (B) and activated PtRu/C (C). Scanning top to middle to bottom, -0.2 to 1.1 to -0.2V with  $\Delta 0.1V$  and reference at -0.25V of the positive (anodic) sweep.

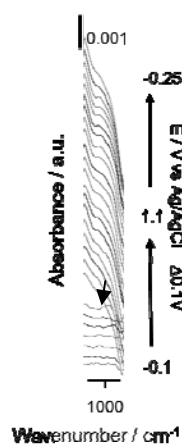


Figure S5: Potential difference spectra of adsorbed MeOH as a function of potential on unactivated PtRu/C. Scanning top to middle to bottom, -0.25 to 1.1 to -0.1V with  $\Delta 0.1V$  and reference at -0.2V of the negative (cathodic) sweep.

### REFERENCES

- (1) Conway, B. E.; Jerkiewicz, G. *J. Electroanal. Chem.* **1992**, 339, 123-146.
- (2) Miyake, H.; Ye, S.; Osawa, M. *Electrochem. Comm.* **2002**, 4, 973-977.