

## Supplementary Information

### **New Approach for Rapidly Determining Pt Accessibility of Pt/C Fuel Cell Catalysts**

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**Materials and chemicals:**

Potassium tetrachloroplatinate ( $K_2PtCl_4$ ,  $\geq 99.9\%$ , metals basis,  $Pt \geq 46.0\%$ ), cetyltrimethylammonium bromide (CTAB, 99%) and sodium borohydride ( $NaBH_4$ , 98 %) were purchased from Aladdin Chemistry Co., Ltd. They were used as raw material without purification.

**Synthesis of Pt/VC and Pt/KB:**

Pt/VC and Pt/KB are prepared using sodium borohydride reduction method reported in the literature.<sup>1</sup> Dissolve 0.0830 g potassium tetrachloroplatinate and add water to obtain 10 g solution, and ageing for 28 h. 0.1458 g of CTAB was dissolved in 10 mL of chloroform, then 0.0225 g of VC was added, and ultrasonicated for 10 min to obtain a uniform dispersion. Then the potassium tetrachloroplatinate aqueous solution was added, and the mixture was stirred at room temperature for 1 hour. After adding 90 mL of water, add 10 g of sodium borohydride aqueous solution (containing 0.1135 g of sodium borohydride), and stir quickly. When no bubbles are generated, filter and collect the product. After washing with ethanol, it dried under vacuum at 80 °C for 6 hours to obtain Pt/VC. Pt/KB can be prepared in the same way, just replace VC carbon black with KB carbon black

**MEA Assembly:**

0.074 g of either Pt/KB or Pt/VC was dispersed in 0.230 mL D2020 perfluorosulfonic acid from Chemours. 9.80 g water/isopropanol (80:20 weight ratio) was then added, followed by ultrasonic treatment for 10 min to obtain a uniform catalyst ink. The cathode catalyst was prepared by spraying this ink directly onto a commercial membrane on a heated vacuum table at 120 °C. The

anode catalyst layer was prepared from the same ink, with a targeted Pt loading of 0.1 mg/cm<sup>2</sup>. Pt loadings were confirmed through XRF measurements. MEAs with an active area of 4 cm<sup>2</sup> were prepared by hot pressing together with the frame (HB-260, Hephas) at 120 °C, 3765 bs, 100 s. The cathode was prepared using a Pt/high surface area carbon (Pt/HSAC) catalyst and D2020 perfluorosulfonic acid from Chemours. The Pt loading was kept constant at 0.35 mg/cm<sup>2</sup>.

### **Physical Characterization:**

Inductively coupled plasma (ICP) analysis was performed using an Agilent ICP-5110 system. 5 mg of the Pt/VC or Pt/KB sample was added to the corundum crucible and placed in a muffle furnace at 800 °C for 30 min. After cooling, added 20 ml of aqua regia and 20 ml of water and heated to dissolve to obtain a clear solution. The solution was collected and diluted to 1 L with deionized water, then tested using the ICP equipment. Pt working curve solutions, using 1 g/L Pt standard solution were prepared and diluted using the same method. The powder X-ray diffractometer (XRD) was tested on the Bruker D8 advance powder X-ray instrument, using Cu Ka radiation. The scanning range is 10-90 °, and the scanning speed is 5 °/min. Pt loadings within the MEAs were verified using X-ray fluorescence (XRF) prior to MEA testing. The nitrogen adsorption-desorption curves are tested on the Micromeritics Tri-Star II 3020 Surface Area and Porosity Analyzer instrument using the samples which were degassed at 150 °C to a constant mass. The mass reductions are considered to be the moisture of the samples.

### **3D-TEM/TEM tomography:**

To allow proper imaging of the samples, special support-grids had to be prepared: Standard TEM grids with a 2x1 mm oval hole were covered with a ~40 nm thin holey carbon film (both EMS, Hatfield, Pennsylvania, USA). Afterward, one drop of Graphene oxide (concentration of 0.1

mg/ml in distilled water, diluted down from 2 mg/ml Graphene oxide from Sigma Aldrich/MilliporeSigma, St. Louis, MO, USA) was put on one side of those grids for 20 seconds and then removed by filter paper. With the other side, the grid was placed on a suspension of fiducial gold (ProteinA gold, bought from the CMC, University Medical Center Utrecht, The Netherlands) for 10 minutes and then moved to two consecutive drops of distilled water for rinsing and then left for an hour to dry. The concentration of the gold suspension and diameter of the gold particles should be adjusted to the desired final magnification of the TEM images and tomograms. In our case, a dilution of 1+4 of the stock fiducial gold solution in water and a diameter of 10 nm was chosen.

The sample powder was suspended in ethanol and sonicated for 5 minutes. A drop of this suspension was placed on the Graphene oxide side of the TEM grid and left to dry for several minutes.

All Transmission Electron Microscopy work was carried out on a Tecnai TF30 G2 FEG-TEM (Thermo Fisher Scientific, Hillsboro, Oregon, USA) at 300 kV acceleration voltage with a model 2040 Dual-Axis Tomography Holder (Fischione Instruments, Export, PA, USA). The images were captured on a Gatan OneView camera (Gatan, Pleasanton, California, USA) at 4096x4096 pixels.

The dual axis tomography was done by taking one image every degree for a tilt range between 130 and 140 degrees with the program SerialEM.<sup>2</sup> The tomographic reconstruction was done by weighted back-projection with the IMOD software package.<sup>3,4</sup> The same software was used for visualization and analysis.

The detached particles observed in the tilt series are the Au fiduciary markers used to improve the final alignment of the 3D reconstruction. They are not part of the sample, but rather, are added to the TEM sample holder during TEM sample preparation.

### **Electrochemical analysis**

Rotating disc electrode (RDE) tests were performed using a Pine Research rotator and gold RDE electrode (5 mm). The ink was prepared by mixing 3 mg of Pt/VC or Pt/KB catalyst with 3 mL of an 80:20 water: isopropanol solution and 30  $\mu\text{L}$  of an 11.6 wt% Nafion aqueous solution. This ink was then sonicated to disperse the catalyst. Two 10  $\mu\text{L}$  aliquots of the ink were then deposited onto the gold electrode, with the first aliquot being allowed to dry under prior to addition of the second. The prepared electrode is immersed in 0.1 M  $\text{HClO}_4$  electrolyte for 1 day to make the catalyst fully wetted. The RDE cell was purged with  $\text{N}_2$  for 60 minutes before beginning the experiments. Prior to evaluating Pt accessibility, voltage cycling was performed from 0.05 to 1.0 vs. a reversible hydrogen electrode (RHE) at 100 mV/s for 20 cycles. This was performed to ensure the catalyst is clean. To evaluate Pt accessibility, cyclic voltammetry was performed from 0.05 to 1.0 vs. RHE with sweep rates of 10 mV/s, 20 mV/s, 50 mV/s, 100 mV/s, 200 mV/s, 400 mV/s, 600 mV/s, 800 mV/s or 1000 mV/s in sequence. At each specified sweep rate, 3 CV cycles were performed.

MEA testing was performed on a Scribner 890e test station. MEAs were conditioned at 100% RH, 136 kPa-a, and 75 °C under air/ $\text{H}_2$  for 15 h prior to testing. Each MEA went through the same conditioning protocol and was fully activated to give consistent BOL performance for two consecutive tests before reversal testing.  $\text{H}_2$ /Air polarization curves were obtained at a fixed flow rate of 1 slpm for  $\text{H}_2$  and 1.8 slpm for Air to evaluate the performance. Cathode CVs were obtained by feeding  $\text{N}_2$  to the cathode and  $\text{H}_2$  to the anode of the MEA, and CO-stripping experiments were performed to determine the electrochemical roughness factor (R.F.) For all tests including reversal

testing, the cell temperature, RH and gas pressures were fixed at 75 °C, 100% and 136 kPa-a, respectively. Mass activities were calculated from the IR-corrected polarization curves obtained under H<sub>2</sub>/O<sub>2</sub> at 75 °C, 100% RH and 136 kPa by dividing the current density at 0.9 V by the Pt loading (Equation 1).

$$\text{Mass Activity} \left( \frac{\text{A}}{\text{mg}} \right) = \frac{\text{Current Density at 0.9 V (IR - corrected)} \left( \frac{\text{A}}{\text{cm}^2} \right)}{\text{Pt Loading} \left( \frac{\text{mgPt}}{\text{cm}^2} \right)} \quad (1)$$

Table S1 ICP, moisture and Pt wt% results of Pt/VC and Pt/KB.

Sample	ICP Pt wt%	Moisture test H <sub>2</sub> O wt%	Calculated value Pt wt%
Pt/VC	45.0	4.95	47.3
Pt/KB	44.1	7.55	47.7

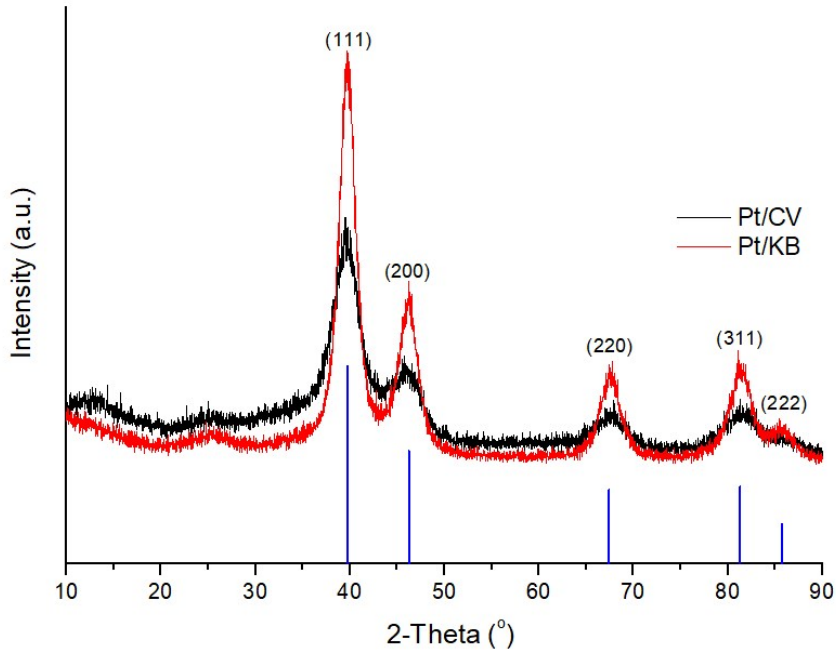


Fig. S1 XRD patterns for Pt/CV (black) and Pt/KB (red). The blue lines are the standard spectrum of Pt (PDF#04-0802).

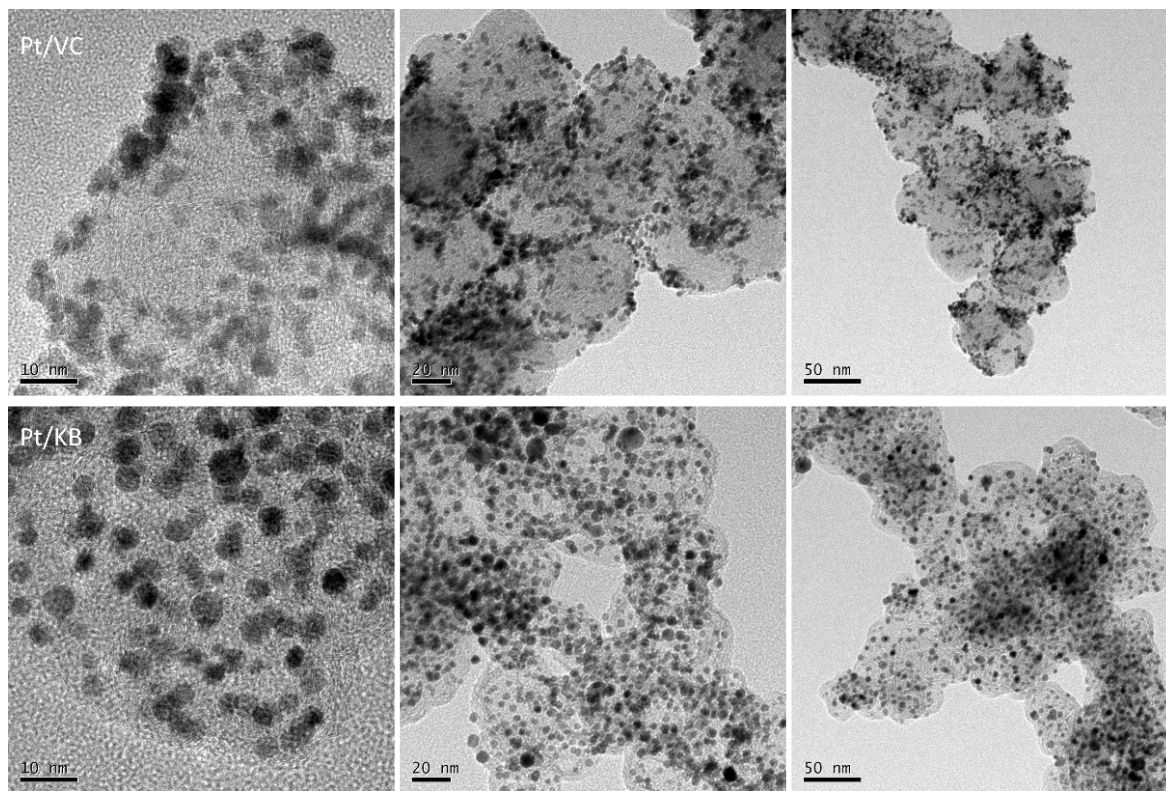


Fig. S2 Conventional TEM images for Pt/VC and Pt/KB with different magnifications.

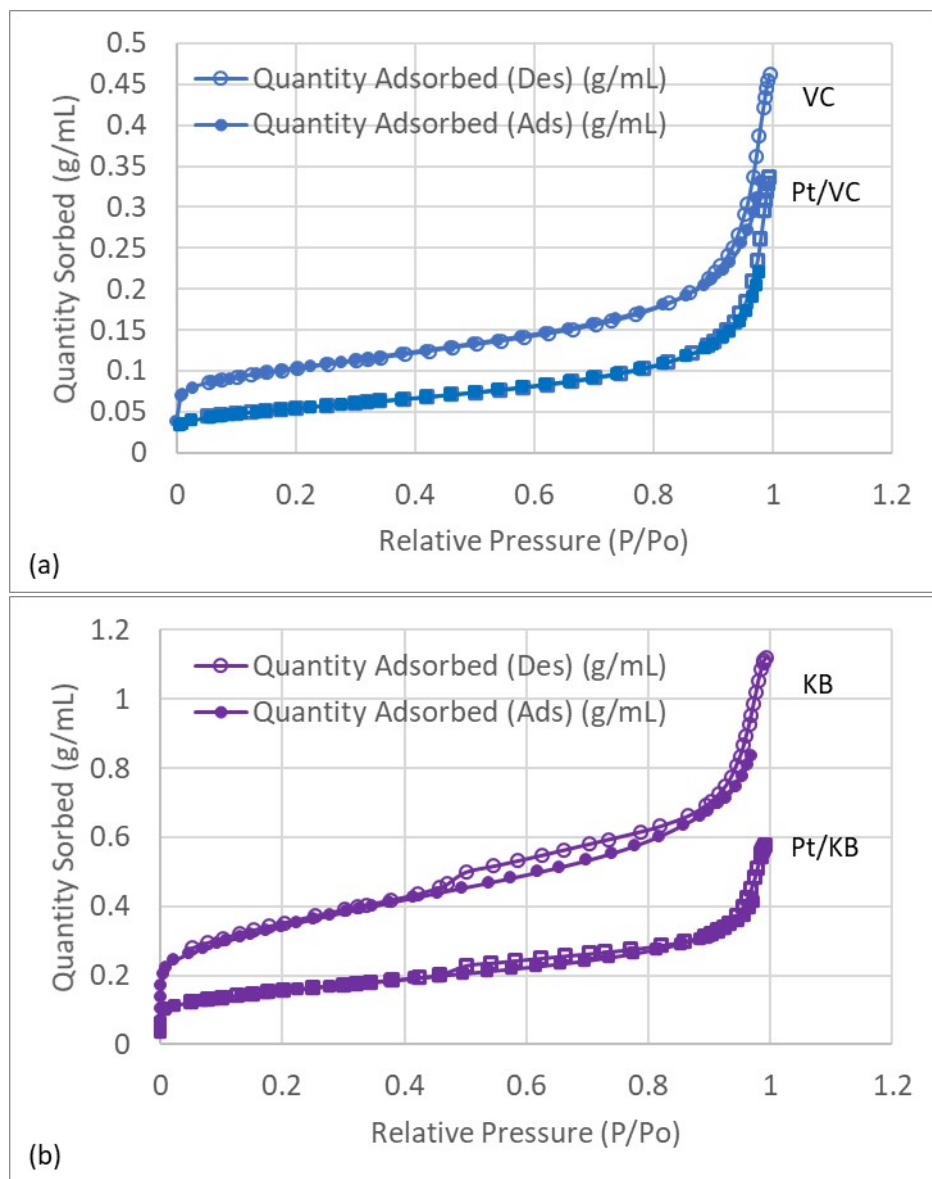


Fig. S3 Nitrogen adsorption-desorption isotherm (a) VC and Pt/VC, (b) KB and Pt/KB.



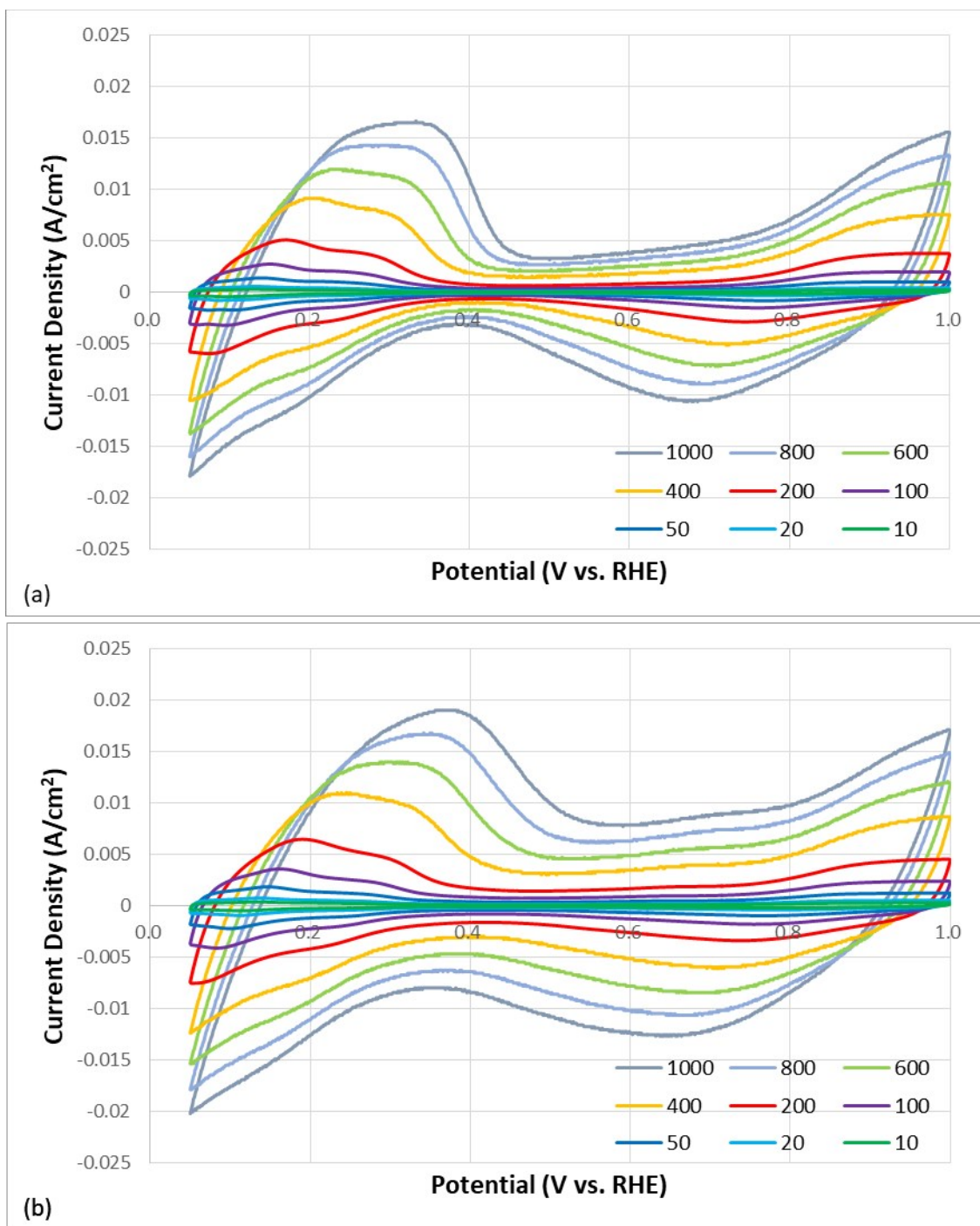


Fig. S4 CV curves under different sweep rates by RDE method for (a) Pt/VC and (b) Pt/KB, under  $N_2$ , in 0.1 M  $HClO_4$ , with electrode rotation speed of 1600 rpm.

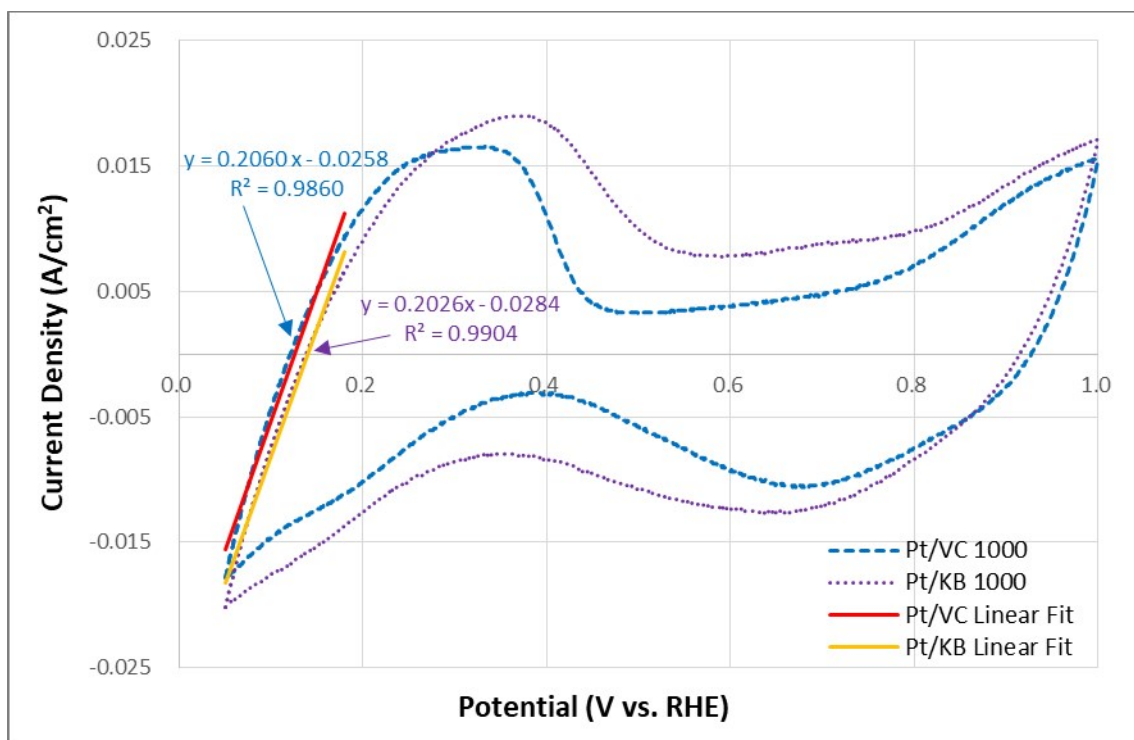


Fig. S5 CV curves under sweep rate of 1000 mV/s by RDE method for Pt/VC (blue dotted line) and Pt/KB (purple dotted line), under  $N_2$ , in 0.1 M  $HClO_4$ , with electrode rotation speed of 1600 rpm. The red and yellow solid lines plotted over a potential range of 0.05-0.18 V represent the resistive distortion to these CVs due to the high (1000 mV/s) sweep rate. The very similar values for the slopes of these two lines is evidence that both catalysts have a similar degree of distortion due to increasing resistance at high scan rates.

#### References:

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