

Electronic Supplementary Information (ESI)

Low loading of Platinum on Transition Metal Carbides for Hydrogen Oxidation and Evolution Reactions in Alkaline Electrolyte

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Experimental methods

Pt supported onto TMC powders: The deposition of 5 wt% Pt on commercially-obtained NbC, VC, WC, TiC, TaC and ZrC (Alfa-Aesar) was achieved via the impregnation method, using 0.05 g of tetraamineplatinum(II) nitrate (Alfa Aesar, Premion) as a precursor dissolved in ~ 5 ml of DI water and added to 0.495 g of different TMC powders. The solution was then stirred for 12 hours at room temperature to ensure the absorption of the precursor onto the support. The solution was then placed in an oil bath and heated to ~330 K for another 12 hours to slowly evaporate the water. The vial was then placed in a furnace and heated to 373 K at 0.4 K/minute and dried for 10 hours. After the catalyst was fully dried, it was ground to a fine powder with a glass rod. The solid was then transferred to a quartz tube furnace to be reduced under H₂ (20 sccm) at room temperature for 30 minutes. The temperature was then increased at 1 K/minute to 563 K and held for 4 hours. The furnace was allowed to cool to room temperature and the catalysts were passivated in 99% N₂ and 1% O₂ (100 sccm) at room temperature for 1

hour.

Electrode preparation: Each Pt/TMC catalyst was dispersed in a solution and sonicated for 20 minutes to prepare well dispersed ink, which is needed to make homogenous thin films on the electrode surface. A specific volume of the ink was dropped on the glassy carbon electrode (GCE, Pine Instruments, 5 mm in diameter). Table 1 summarizes the ink recipes used for the preparation of the electrodes. For some of the catalysts, specifically 5% Pt/NbC and 5% Pt/TiC, more than one drop of catalyst was required due to the nature of the solvent. In between each drop, the electrode was allowed to dry completely before the next drop was deposited. In the case of Pt/TiC, where ethylene glycol was used as the solvent, the solvent was evaporated by drying the electrode in an oven at 100 °C for 1 hour. As a benchmark reference, commercial 46% Pt on carbon (Pt/C, TKK) was prepared by mixing 1.49 mg of Pt/C in 10 ml of DI water and 10 μ l of the ink was deposited on the glassy carbon electrode.

Table 1. Ink recipes used for 5 wt% Pt/TMC catalysts.

Catalyst	mg _{catalyst} /mL _{ink}	Solvent	Drop Vol. (μ l)	μ g _{metal} /cm ² _{disk}	μ g _{support} /cm ² _{disk}
5% Pt/NbC	17.4	100% iso	3 (x3)	40	760
5% Pt/TaC	15.7	50%iso+50%H ₂ O	10	40	760
5% Pt/TiC	7.8	100% EG	10 (x2)	40	760
5% Pt/VC	15.7	50%iso+50%H ₂ O	10	40	760
5% Pt/ZrC	15.7	50%iso+50%H ₂ O	10	40	760
5% Pt/WC	15.7	50%iso+50%H ₂ O	10	40	760

Electrochemical measurements: The electrochemical activities of these powders were characterized in a traditional three cell configuration in 0.1 M KOH at room temperature, using linear sweep voltammetry

(LSV). A Pt wire was used as a counter electrode and a saturated double-junction Ag/AgCl (0.197 V from NHE, Pine Research Instrumentation) was used as a reference electrode. The Pt/TMC and 46% Pt/carbon powders were conditioned by cycling 25 times from -0.9 V to 0 V vs. Ag/AgCl saturated with Ar at a rate of 50 mV s⁻¹ before LSV measurements until steady state was reached. Butler-Volmer and Tafel plots were generated from LSV scans that were recorded for the powder samples at a scan rate of 10 mV s⁻¹ in saturated with H₂.

Catalysts characterization: The morphological characteristics of the synthesized catalysts and their particle sizes were analyzed by transmission electron microscopy (TEM) measurements. The JEOL TEM-2100F TEM instrument was used. Due to the difficulty of obtaining electrochemically active surface areas through the integration of the hydrogen under potential deposition (HUPD) region of Pt in the Pt/TMC samples, copper stripping was used instead.¹ The following procedure was implemented for all Cu stripping experiments: First, the Pt/TMC electrode was placed in a three-electrode cell configuration containing 0.5 M H₂SO₄ and cycled 25 times from -0.9 V to 0 V vs. Ag/AgCl to clean the Pt surface. The potential was then held at 0.25 V vs. RHE for 60 seconds. Using LSV, the potential was immediately scanned from 0.25 V to 0.8 V vs. RHE after equilibration to obtain the background current. The electrode was then transferred to a separate cell containing 0.5 M H₂SO₄ and 2 mM CuSO₄. The same equilibration and LSV procedures were then performed in the presence of Cu²⁺ ions to obtain the Cu stripping curve. To find the total charge transferred in the Cu stripping process, the charge density of 420 μC/cm²_{Pt} was used,¹ and the background current was subtracted from the Cu stripping curve.

References

1 C.L. Green, A. Kucernak, *The Journal of Physical Chemistry B*, 2002, **106**, 1036.

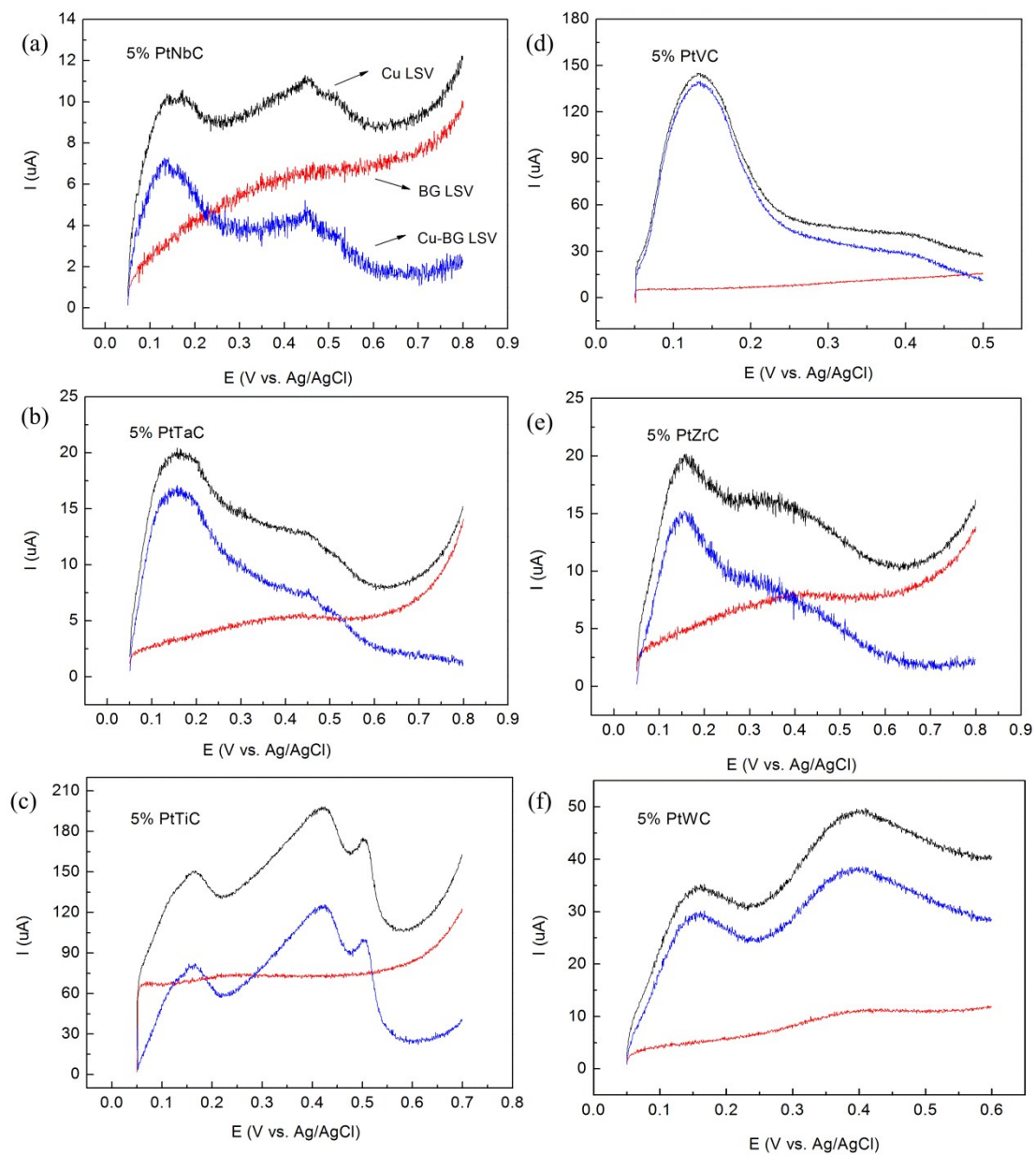


Fig.1 LSVs of copper stripping for each Pt/TMC catalyst (the black line). Each LSV has the background current subtracted (the blue line). The red lines are the background LSVs. Each catalyst displays the general copper stripping features of Cu.

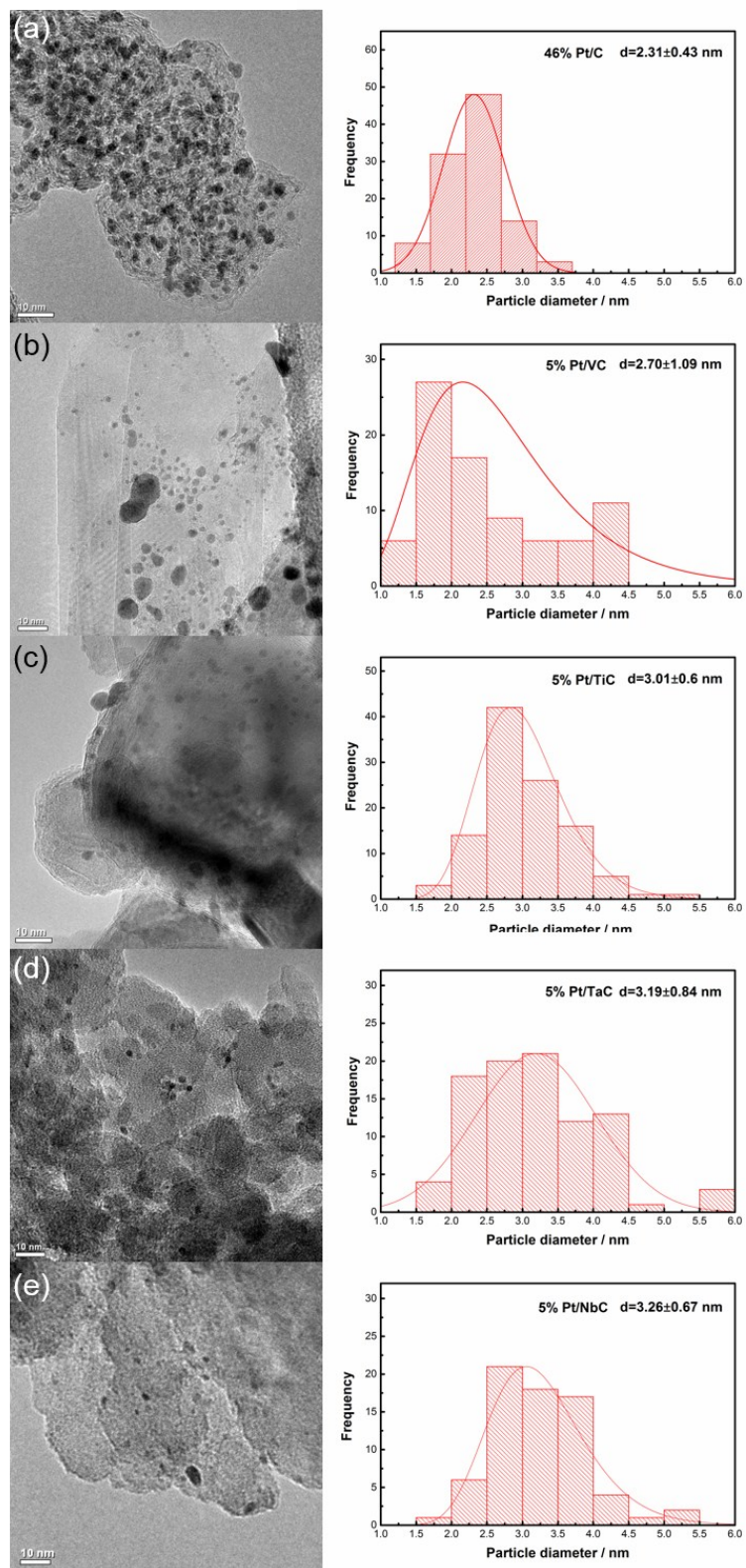


Fig.2 TEM images and the corresponding histogram for the Pt/TMC catalysts.

(a) the commercial 46% Pt/C (b) 5% Pt/VC (c) 5% Pt/TiC (d) 5% Pt/TaC (e) 5% Pt/NbC.