Rational growth of Pt particles using ED of Pt on Pt/XC72 and evaluation for the oxygen reduction reaction (ORR) in PEM fuel cells

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Motivation

In catalysis, the performance of catalytic system has a strong dependence on the size of the metal nanoparticles. The key relationship between catalytic activity and the size of the metal nanoparticles due to the selective exposure of different facets (Figure 1) and their effect on the adsorption strength of reactants.

- Control of supported metal nanoparticle size and accurate characterization are crucial in catalyst design to obtain optimized performance.

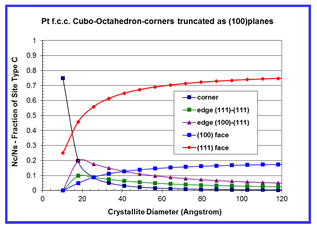


Figure 1. Pt facet distribution as a function of size, based on[1]

Hypothesis

Conventional preparation method (simple impregnation) results in larger particles, as shown in Figure 2 a and b. SEA has been shown to produce ultra-small particles with narrow size distributions and uniform densities on the support surface, as shown in Figure 2 b and d.

- Hypothesis of using a combination of SEA and ED, both methods using the same metal salt to precisely control sizes of supported nanoparticles while maintaining tight size distributions and spatial separations.

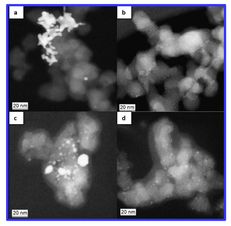


Figure 2. a: 3.0% Ru, DI preparation;
b: 3.0% Ru, SEA preparation;
c: 1.6% Ni, DI preparation;
d: 1.6% Ni, SEA preparation.[2]

Catalyst preparation

1,Strong Electrostatic Adsorption (SEA)

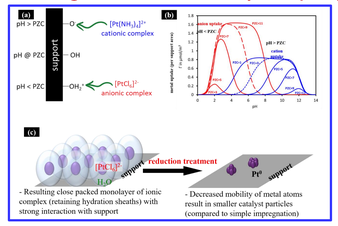


Figure 3. SEA process: (a) PZC determination, (b) uptake-pH survey, (c) Reduction to retain high dispersion

2, Electroless Deposition (ED)

Electroless deposition (ED) is a catalytic or autocatalytic reaction in which a metal precursor is chemically reduced and deposited onto a pre-existing metal(base metal).

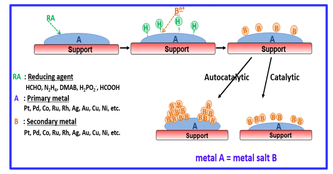


Figure 4. ED process with the same metal salt as SEA

Pt particle characterization by STEM and XRD

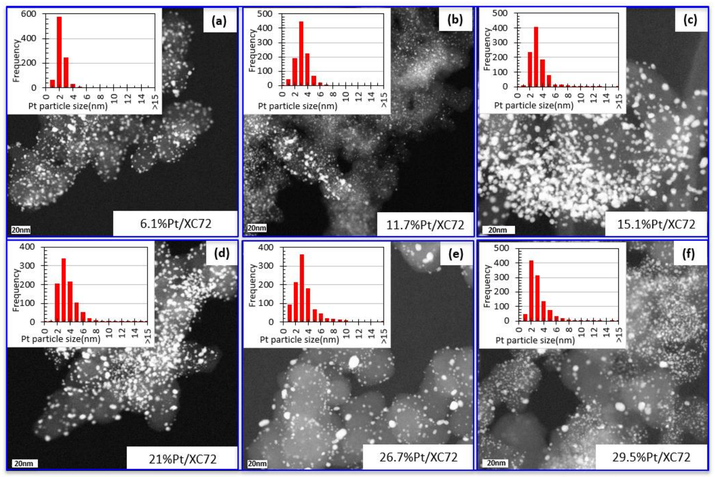


Figure 5. STEM micrographs and corresponding size distributions of (a) 6.1% Pt/VXC72, (b) 11.7% Pt/VXC72, (c) 15.4% Pt/VXC72,(d) 21% Pt/VXC72 ,(e) 26.7%Pt/VXC72 and (f) 29.5%Pt/XC72

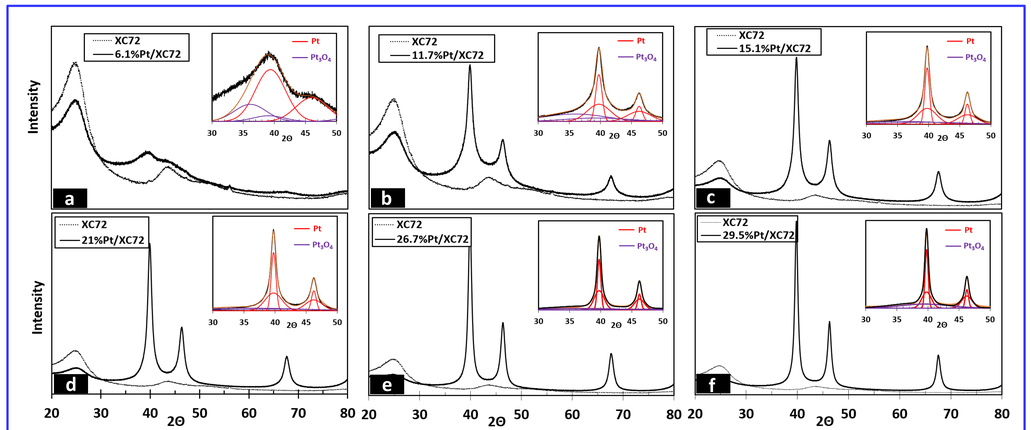


Figure 6. XRD profiles with deconvoluted patterns of (a) 6.1% Pt/VXC72, (b) 11.7% Pt/VXC72, (c) 15.4% Pt/VXC72,(d) 21% Pt/VXC72 ,(e) 26.7%Pt/VXC72 and (f) 29.5%Pt/XC72

Conclusions

- Combination of SEA and ED preparation have provided more effective way to synthesize Pt catalysts with variable particle sizes by using ED of Pt on highly dispersed Pt particles fabricated by SEA.
- Particle size measurements from XRD, chemisorption and STEM mainly agree with each other. Electrochemical surface area (ECSA) calculation also agree with other particle size measurements.
- ORR evaluation demonstrates that specific activity is a function of Pt particle size, as a structure sensitive reaction.

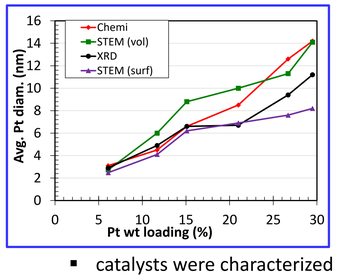
Future Work

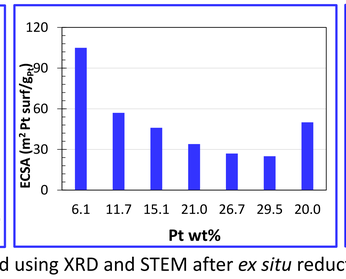
- Switching from semi-continuous ED to continuous ED to deposit Pt in better thermal and kinetic controllable way.
- SEA works for many VIII and IB metals and ED has same versatility, like Pd, Rh, Co, Ni, Au, Cu, Ag, Ru, Ir. More metals are possible to control growth by SEA and ED combination.

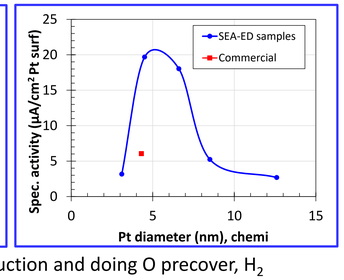
Pt particle size comparison and Oxygen Reduction Reaction(ORR) evaluation

Table 1: Comparison of particle size from XRD, Chemisorption and STEM surface/volume average size, and ECSA, specific activity result.

catalyst information			particle size determination				Electrochemical evaluation	
Base catalyst	Pt wt% added by ED	total Pt wt%	d_{Pt} XRD (nm)	$d_{Pt,}$ Chemi (nm)	$\bar{d}_{Pt}$ from STEM $\bar{d}_s$ (nm)	$\bar{d}_{Pt}$ from STEM $\bar{d}_v$ (nm)	ECSA (m^2 Pt surf/g_{Pt})	specific ORR activity @ 0.9V ($\mu A/cm^2_{Pt}$)
6.1% Pt on VXC-72(by SEA)	0.0	6.1	2.9	3.1	2.5	2.7	105	3.2
	5.6	11.7	4.9	4.5	4.1	6.0	57	19.7
	9.0	15.1	6.6	6.6	6.2	8.8	46	18.0
	14.9	21.0	6.7	8.5	6.9	10.0	34	5.2
	20.6	26.7	9.4	12.6	7.6	11.3	27	2.7
	23.4	29.5	11.2	14.2	8.2	14.1	25	--
commercial	n/a	20.0	3.2	4.3	--	3.1	50	6.1







- catalysts were characterized using XRD and STEM after *ex situ* reduction and doing O precover, H_2 titration after *in situ* reduction.
- Pt particle size matches with each other for this 3 characterization methods and agrees with ECSA, smaller particle has higher ECSA.

Reference

[1] Van Hardeveld, R.; Hartog, F., Influence of Metal Particle Size in Nickel-on-Aerosil Catalysts on Surface Site Distribution, Catalytic Activity, and Selectivity. In *Advances in Catalysis*, Academic Press: 1972; Vol. 22, pp75-113.

[2] Mehrabadi B.A.T.; Eskandari S.; Khan U.; White R. D.; Regalbuto J. R., A Review of Preparation Methods for Supported Metal Catalysts. In *Advances in Catalysis,* Academic Press, 2017, pp. 1-35.