Stability of platinum nanoparticles supported on nitrogen-doped carbon

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Motivations

- Ultra-small platinum nanoparticles (Pt-NPs) of high metal dispersion are desirable in many oxidative reactions such as oxygen reduction reaction (ORR) in fuel cells, methanol oxidation etc.
- Carbon supported Pt-NPs (Pt/C) are considered the most effective catalysts for such reactions since Pt can be highly dispersed on carbon.
- However, at oxidative environment, the ultra-small Pt-NPs are quickly oxidized and form oxide films on the metal surface that can decrease the overall performance of the catalysts.
- Literature also agrees that Pt-NPs is intended to separate from carbon support and aggregate into larger particles, owing to Ostwald ripening effects, thus resulting in short-term stability.
- Stabilizing carbon support can improve metal-support interactions to a great extent.
- Nitrogen doping into the carbon is one of the promising techniques for stabilizing support, as well as supported NPs.

Methodology

MATERIALS

- **Support:** One N-free-C and two N-doped-C (one is prepared by Savannah River National Laboratory and other is made by Virginia Commonwealth University).
- **Precursor:** Hexachloroplatinum complex (Sigma Aldrich)

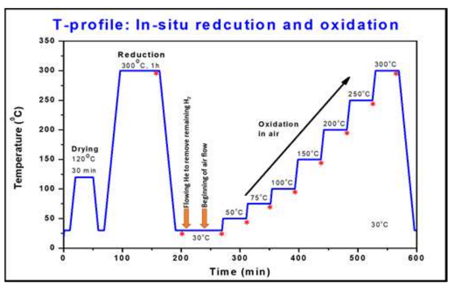
Support	SA (m^2/g)	SEA pH	Max. uptake (μmol/m^2)	Max. Pt loading
BP-2000	1400	2.75	0.81	24%
N-doped C (SRNL)	900	1.5	0.81	16%
N-doped C (VCU)	2250	1.5	0.78	35%

CATALYST PREPARATION & CHARACTERIZATOPM

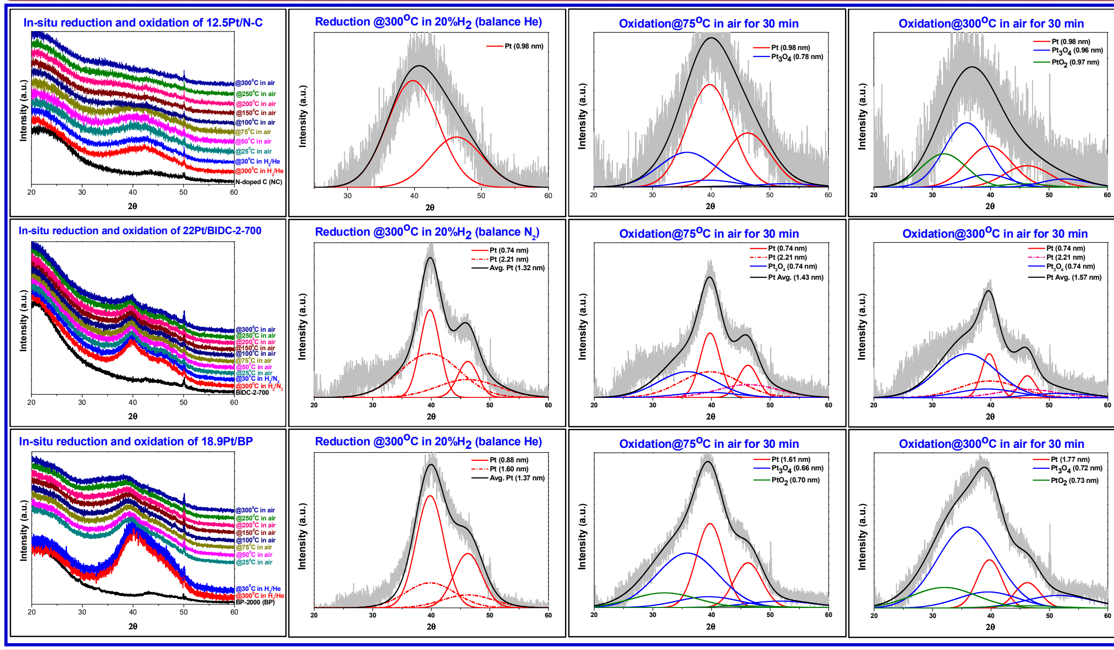
- **Preparation:** Strong Electrostatic adsorption (SEA)
- **Characterization:** In-situ X-ray diffraction (XRD) and Screening electron transmission microscopy (STEM)

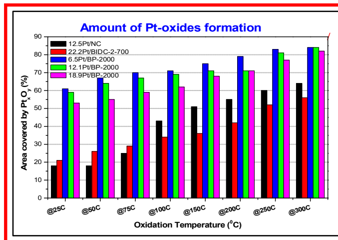
In-situ XRD: Reduction and Oxidation

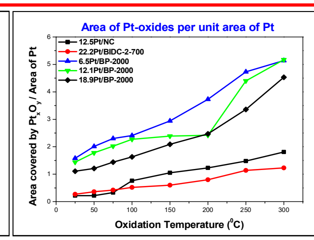
- **Reduction:** @300^{0}C for 1h in 20% H_2 / N_2.
- **Oxidation temperature:** 25^{0}C to 300^{0}C.
- **XRD Scanning rate:** 3^0/min
- **Holding time at each temperature:** 30 minutes



Results and discussions

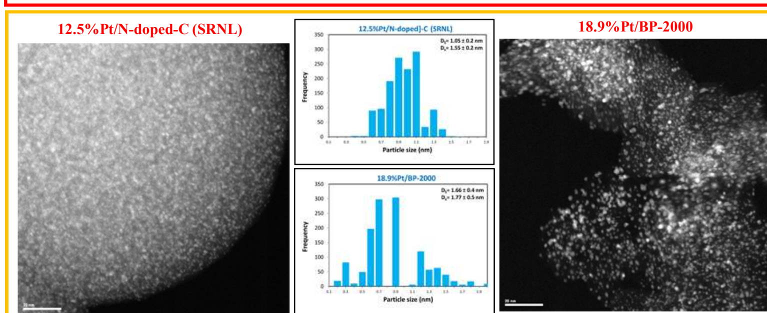






Particle size calculated from In-situ XRD data

		Pt^0 (nm)	Pt_3O_4 (nm)	PtO_2 (nm)
12.5Pt/N-C (SRNL)	@25^{0}C	0.98	0.73	-
	@300^{0}C	0.98	0.97	0.96
12.1Pt/BP-2000	@25^{0}C	1.30	0.73	0.66
	@300^{0}C	1.77	0.79	0.79
18.9Pt/BP-2000	@25^{0}C	1.58	0.70	0.66
	@300^{0}C	1.77	0.73	0.77
22Pt/N-C (VCU)	@25^{0}C	1.4	0.73	-
	@300^{0}C	1.6	0.73	-



Conclusion and Future works

- Pt^0 NPs are immediately oxidized even exposure to air at room temperature.
- N-doped-C supported Pt-NPs show lower tendency for oxidation compared to N-free carbon supported Pt-NPs.
- At 25^{0}C in air, the rate of oxidation of Pt/BP-2000 is more than twice compared to Pt/N-doped-C.
- At 300^{0}C in air, 40-50% of N-doped-C supported Pt-NPs remain in metallic while more than 85% of Pt-NPs supported on BP-2000 are oxidized.
- Between two N-doped carbons, VCU carbon is more effective to stabilize Pt-NPs in oxidative conditions.
- As STEM shows, N-doped-C supported NPs are more uniformly distributed than N-free-C supported NPs
- STEM is needed for Pt/N-doped-C (VCU) in order to compare between the N-doped-carbons.
- Evaluate catalyst performance for oxygen reduction in Proton-exchange membrane fuel cells.

References

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Acknowledgment

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