Stability of platinum nanoparticles supported on nitrogen-doped carbon

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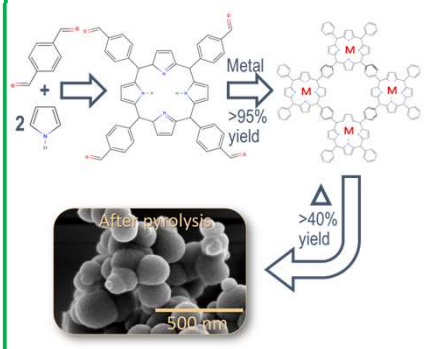
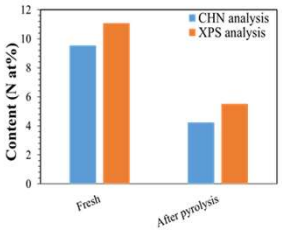
Motivations

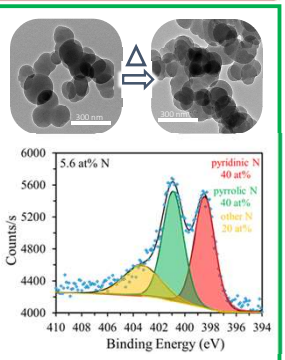
- Ultra-small platinum nanoparticles (PtNPs) of high metal dispersion are desirable in many oxidative reactions such as oxygen reduction reaction (ORR) in fuel cells, methanol oxidation etc.
- Carbon supported PtNPs (Pt/C) are considered the most effective catalysts for such reactions since Pt can be highly dispersed on carbon.
- However, at oxidative environment, the ultra-small PtNPs are quickly oxidized and form oxide films on the metal surface that can decrease the overall performance of the catalysts.
- Literature also agrees that PtNPs is intended to separate from carbon support and aggregate into larger particles, owing to Ostwald ripening effects, thus resulting in short-term stability.
- Improvement of carbon support may enhance support-metal interactions.
- Nitrogen-doped carbon (N-doped C) has attracted the highest attention due to its high interactions with metals.

Preparation of nitrogen-doped Carbon





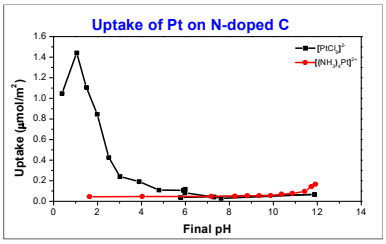
After pyrolysis, the nitrogen content decreases by half as confirmed by CHN and XPS analysis



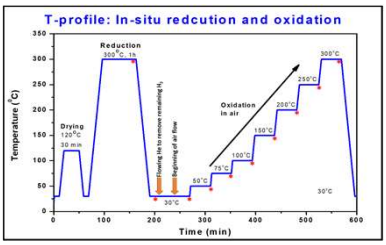
Methodology

- Nitrogen was doped into Benzene-1,4-dialdehyde by high-temperature pyrolysis.
- Catalysts were prepared by strong electrostatic adsorption (SEA).

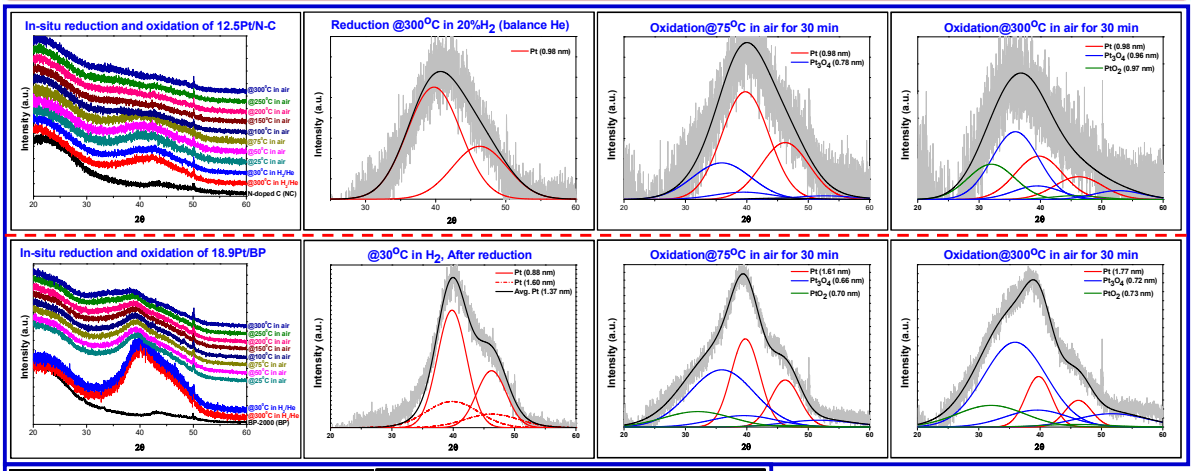
Support	Surface area (m^2/g)	SEA pH	Maximum Metal loading
BP-2000	1400	2.75	24%
N-doped C	900	1.5	16%

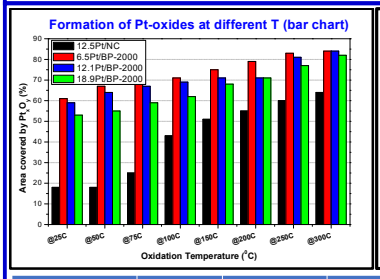


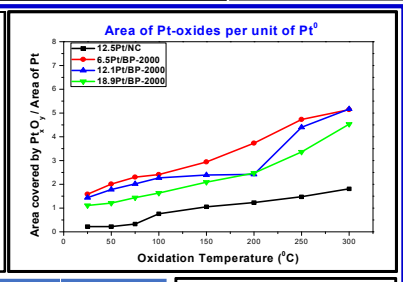
- Catalysts were reduced and oxidized in in-situ XRD equipment.
  - Reduced @300^{0}C f for 1h in 20% H_2 / N_2.
  - Oxidized at different temperature from 25^{0}C to 300^{0}C.
  - XRD Scanning rate: 3^0/min
  - Temperature kept constant for 30 minutes prior to measurement



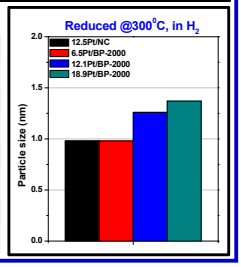
Results and discussions







		Pt^0 (nm)	Pt_3O_4 (nm)	PtO_2 (nm)
12.5Pt/NC	@25^{0}C	0.98	0.73	-
	@300^{0}C	0.98	0.97	0.96
6.5Pt/BP-2000	@25^{0}C	0.98	0.72	0.66
	@300^{0}C	0.98	0.84	0.77
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



Conclusion

- No Pt-oxides have found after reduction at 300^{0}C, but Pt^0 immediately oxidized and form both PtO_2 and Pt_3O_4 when air was flown across the catalysts, even at room temperature.
- The rate of oxide formation is higher for Pt/BP-2000 compared to Pt/N-doped carbon at any temperature (in presence of air flow), and this difference is very significant till 100^{0}C.
- After oxidation @300^{0}C in air, less than 18% of Pt has seen as metallic form for BP-2000 supported catalysts while it is 36% for Pt/N-doped carbon.
- For BP-2000 supported catalysts, the size of PtNPs is increasing with increasing metal loading on support, thus decreasing the rate of initial oxidation.

Future works

- Screen Transmission Electron Microscopy (STEM) imaging will be used to
  - Confirm the crystallographic phases of catalysts nanoparticles.
  - Determine the size of NPs and investigate how Pt-oxides are staying with Pt^0.
  - Confirm particle size distribution
- Evaluate catalyst performance for oxygen reduction in Proton-exchange membrane fuel cells.

Acknowledgment

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References

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