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BSc (Chemistry), Dalhousie University, 2010

DEPARTMENT OF CHEMISTRY

TITLE OF THESIS: EFFECTS OF SURFACE STRUCTURE ON THE
ELECTROCATALYTIC ACTIVITY OF PT-
BASED NANOPARTICLES: AN X-RAY
ABSORPTION SPECTROSCOPY STUDY

TIME/DATE: 2:00 pm, Thursday, September 22, 2016

PLACE: Room 3652, The Life Sciences Centre, 1355
Oxford Street

EXAMINING COMMITTEE:

Dr. Aicheng Chen, Department of Chemistry, Lakehead University
(External Examiner)

Dr. Heather A. Andreas, Department of Chemistry, Dalhousie University
(Reader)

Dr. Mark N. Obrovac, Department of Chemistry, Dalhousie University
(Reader)

Dr. Mary Anne White, Department of Chemistry, Dalhousie University
(Reader)

Dr. Peng Zhang, Department of Chemistry, Dalhousie University
(Supervisor)

DEPARTMENTAL REPRESENTATIVE: Dr. Erin R. Johnson, Department of Chemistry,
Dalhousie University

CHAIR: Dr. Marilyn Macdonald, PhD Defence Panel,
Faculty of Graduate Studies

ABSTRACT

With clean and renewable sources of energy being a major focus for modern societies, developing efficient means of energy storage is a necessity. Of the technologies currently available, electrochemical fuel cells stand to benefit most from advances in nanomaterials research, due to their reliance on (often Pt-based) electrode catalysts. Perhaps the greatest advantages of using nanoparticle electrode catalysts is their large specific surface area.

While structural characterization of nanoparticles (particularly their surface structure) can be a significant challenge, the use of X-ray absorption spectroscopy (XAS) can allow researchers to study samples beyond the scope of other techniques. Herein, a series of Pt-based nanoparticles is characterized through a combination of XAS techniques and other complementary methods of analysis in order to study the relationships between their surface structure and electrocatalytic activity.

Following a brief exploratory study on the ability of XAS techniques to elucidate the structure of small Pt nanoclusters, focus is shifted to the preparation and electrocatalytic application of bimetallic Pt nanoparticles containing 3d, 4d, and 5d transition metals (Fe, Ag, and Au, respectively). The first attempts to characterize the structure of Pt-FeO_x nanoparticles revealed a predominantly Pt core coated with Fe oxide rather than the anticipated intermetallic PtFe surface.

While this Pt-core/FeO_x shell structure is poorly suited to catalytic applications, subsequent experiments revealed that this oxide coating was removed during electrochemical cycling to expose a highly active Fe-modified Pt surface. However, the large amount of inaccessible Pt located in the cores of these nanoparticles renders them less than ideally suited for catalytic applications. In order to achieve better surface localization of Pt, AgPt nanoparticles are next prepared via galvanic reaction of a Pt precursor salt with Ag nanoparticles. Those AgPt nanoparticles with the lowest Pt contents are found to have surfaces bearing few-atom Pt clusters, but are unstable under the electrocatalytic conditions; a more electrochemically stable elemental composition is clearly required.

Finally, a synthesis employing simultaneous reduction of Pt and Au precursors results in PtAu nanoparticles with few-atom Pt surface clusters that are both stable and highly active.