

MSE-Colloquium@NTU

10 April 2017, 4.00 pm

Lecture Theatre 7, Nanyang Technological University



Platinum Electrochemistry and Electrocatalysis: Unraveling the Origins of Its Unique Behavior

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About the Talk

In the hydrogen economy involving electrochemical technologies, electrical energy is converted to chemical energy (H_2 , a stable, reusable product) in water electrolyzers and such generated H_2 is used to produce electrical energy in hydrogen fuel cells. It is a wonderful cycle, in which water is initially a reactant and eventually a product. The processes occurring in water electrolyzers and hydrogen fuel cells, hydrogen evolution (HER), oxygen evolution (OER), hydrogen oxidation (HOR) and oxygen reduction (ORR) reactions, drive an interest in the hydrogen and oxygen electrochemistry and electrocatalysis. Platinum is the most effective electrocatalyst in these reactions, but the origin of its unique activity is poorly understood. However, its exceptional electrocatalytic activity needs to be explained in order to develop guidelines for the design and fabrication of non-noble electrode materials possessing similar properties. The contribution focuses on three phenomena taking place at Pt electrodes: (i) the under-potential deposition of H (UPD H); (ii) surface oxide growth; and (iii) Pt and Pt surface oxide dissolution.

Electrochemical, analytical and surface science research sheds new light on the unique interfacial behavior of Pt in aqueous electrolyte solutions. Temperature-dependent cyclic-voltammetry studies combined with theoretical data treatment facilitate the determination of thermodynamic state functions of UPD H ($\Delta_{ec-ads}G^\circ$, $\Delta_{ec-ads}S^\circ$, $\Delta_{ec-ads}H^\circ$) and the Pt- H_{UPD} surface bond energy ($E_{Pt-H_{UPD}}$). The data show that on a thermodynamic basis H_{UPD} is equivalent to H_{chem} , and suggest that H_{chem} and H_{UPD} occupy the same surface adsorption sites and are embedded in the Pt surface lattice. Electrochemical quartz-crystal nanobalance (EQCN) analysis of interfacial mass changes in the potential range of UPD H and HER reveals the existence of potential of minimum mass (E_{pmm}), the value of which coincides with the completion of a saturation layer of H_{UPD} and the onset of HER. It is observed that HER does not take place on bare Pt but on Pt modified with a layer of H_{UPD} , which modifies the electrode's interfacial wetting ability making the surface hydrophobic-like. The discharge of H_3O^+ in HER or the dissociative adsorption of $H_2(g)$ in HOR proceed easily on Pt than on other metals because the species do not have to displace H_2O molecules or hydrated ions due to weak surface dipole- H_2O dipole and surface dipole-hydrated ion interactions. Effective and cheap non-Pt electrocatalysts for HER and HOR should mimic the interfacial behavior of Pt; thus, they should: (i) be chemically and mechanically stable; (ii) adsorb H ; (iii) dissociate H_2 ; and (iv) have weak interactions with H_2O molecules and hydrated ions. The electro-oxidation of Pt at well-defined conditions, i.e. polarization potential (E_p), polarization time (t_p), and temperature (T), leads to very thin oxide layers. Their surface chemical composition is analyzed using X-ray photoelectron spectroscopy (XPS) and reveals that PtO is the main species formed at $E_p < 1.60$ V. Application of higher potentials leads to slow growth of PtO₂ on top of the PtO layer. Treatment of the Pt oxide growth employing oxide-growth theories results in the evaluation of the reaction's mechanism and kinetics. Formation of Pt surface oxides is accompanied by their slow but unavoidable dissolution. Stability of Pt oxides depends on the potential that they experience, exposure time, and electrolyte composition and concentration. Electrochemical and chemical Pt and Pt oxide dissolution pathways are discussed.

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Gregory Jerkiewicz received his dual accreditation Master's degree in Chemical Engineering-Engineering Chemistry from the Gdask University of Technology, Poland, in 1984. He also studied solid state physics at the same university (1983-1985). In 1985, he immigrated to Canada and settled down in Ottawa, where he completed his Doctorate (1991) at the University of Ottawa under the supervision of the late Prof. Brian E. Conway (FRSC), one of the icons of electrochemistry of the XX century. Following the doctoral studies, he spent the summer of 1991 working in the Institute of Physics, the University of Fribourg, Switzerland. He joined the Department of Chemistry, Université de Sherbrooke, as a research associate in September 1991 and became Assistant Professor in June 1992. He was promoted to Associate Professorship with tenure in June 1997. In 1997, he won the Electrochemistry Award of the Société Française de Chimie, the first time ever awarded to a researcher residing outside of France. In June 2002, he joined the Department of Chemistry, Queen's University, first as a tenured Associate Professor; he was promoted to the rank of Professor in 2005. In 2004, he was awarded the W. A. E. McBryde Medal of the Canadian Society for Chemistry in recognition of his contributions to interfacial electrochemistry and of his advancement of the electrochemical quartz-crystal nanobalance (EQCN). He has authored over 100 publications that include peer-reviewed papers (88), peer-reviewed book chapters (6), papers in volumes of conference proceedings (24), editorials and prefaces (4), and has co-edited one (1) book and three volumes (3) of conference proceedings. He has delivered over 150 invited keynote lectures, seminars, and conference presentations, and over 230 contributed conference presentations. He has been an active member of several professional associations (the International Society of Electrochemistry, the Electrochemical Society, the Canadian Society for Chemistry) and has served on several executive committees (CSC, ECS – Canadian Section). He was Section Editor of the Canadian Journal of Chemistry and is Editor-in-Chief of Electrocatalysis. In 2012, the President of Poland, Mr. Bronislaw Komorowski, conferred on him the Knight's Cross of the Order of Polonia Restituta in recognition of his outstanding contributions to the Polish society in the 1980s.



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