22ª Reunião Anual de Usuários do LNLS

A 22ª Reunião Anual de Usuários (RAU) do Laboratório Nacional de Luz Síncrotron (LNLS) foi realizada nos dias 28 e 29 de fevereiro de 2012, em Campinas, SP, no hotel **Premium Norte**.

A RAU tem como objetivo fomentar o debate, a troca de experiências e consolidar a comunidade de usuários do LNLS. Trata-se de um importante fórum para discussão, avaliação e de apresentação de propostas de melhoria da infraestrutura de pesquisa e da instrumentação científica da Fonte Síncrotron, e uma oportunidade para troca de informações sobre as pesquisas realizadas nas instalações.

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09/04/12

Effects of Temperature and Chemical Environment in the Electronic Properties of Pt/C and PtRu/C Electrocatalysts

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Bi-metallic Pt alloys have been the subject of intensive investigations as electrocatalysts for low temperature fuel cell reactions, such as the hydrogen oxidation reaction (HOR) in the presence of CO. Besides changes in the reaction mechanism, modifications induced by a second metallic element (typically Ru and Mo) include changes in the Pt electronic structure, which may affect the adsorption characteristics of the Pt atoms. In situ X-ray absorption spectroscopy (XAS) measurements have been used to probe these catalyst electronic changes, but the correlations of this phenomenon with the alloy composition and the understanding of the role of temperature and of the external chemical environment have been not so often discussed. This work presents results of in situ XAS investigations of Pt/C and PtRu/C electrocatalysts, working under the polymer electrolyte fuel cell experimental conditions. The XAS spectra were collected at three distinct temperatures (313, 328 and 353 K), with the catalysts exposed to different gases and fluxes (Argon, Nitrogen, Hydrogen, and CO) at a constant applied potential (100 mV vs. RHE). Together with the XAS experiments, CO stripping voltammetry and HOR polarization measurements were conducted at the same experimental conditions, as described above. The results evidence a decrease of the vacancy of the Pt 5d electronic states with the increase of temperature, in accordance with the Fermi-Dirac distribution theory. This phenomenon explains the small contribution of the electronic effect in the CO tolerance properties of PtRu/C electrocatalysts at high temperatures, as indicated by the polarization measurements. There is an increase of the Pt 5d band occupancy when the catalysts are exposed to hydrogen in comparison to argon, and this is more pronounced for Pt/C than for PtRu/C, probably because the PtRu atoms are reduced during the exposition to H_2. In contrast, the presence of CO leads to an emptying of the Pt 5d band, probably due to the Pt-CO back-bonding, which involves electron donation from Pt to CO. There is no significant temperature effect on the Pt 5d band occupancy for both Pt/C and PtRu/C when exposed to CO. This result corroborates the lower CO coverage observed at higher temperatures, as evidenced by the CO stripping voltammetry and single cell polarization data.

Acknowledgements: The authors thank FAPESP, CNPq, CAPES for financial supports, and Brazilian Synchrotron Light Laboratory (LNLS) for the XAS measurements.