

Atividade de catalisadores de metais não nobres em processos eletroquímicos de conversão de energia: as reações de redução de oxigênio, água e gás carbônico

Activity of non-noble metals catalysts in electrochemical energy conversion processes: oxygen, water and carbon dioxide reduction reactions

Wanderson O. Silva, Ulisses A. Rêgo, Edson A. Ticianelli

Instituto de Química de São Carlos, Av. Trabalhador São-carlense, 400 – São Carlos – SP - Brasil

Resumo: This presentation discusses the performance of carbon and iron based electrocatalysts submitted to different nitriding processes, for the promotion of the oxygen, water and carbon dioxide reduction reactions in different electrolytes. The catalysts have been prepared using carbon powder supports, which are impregnated with the Fe^{2+} (2,4,6-Tris (2-pyridyl)-1,3,5-triazine)₂ complex ($[\text{Fe}(\text{TPTZ})]^{2+}$) and then treated at different temperatures in the range of 700-950 °C, in nitrogen and ammonium atmospheres. Catalysts have been designated as Fe/NC(N₂) and (Fe/NC(NH₃)) for the materials treated under nitrogen and ammonia, respectively; an iron-free nitrogen-doped carbon electrocatalyst (NC(NH₃)) has been used for comparisons. All materials have been characterized by X-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), High angle annular dark field STEM (HAADF-STEM), and energy dispersive spectroscopy (EDS), while the electrochemical investigations have been performed with the catalytic materials forming thin films deposited on glassy carbon disc and carbon cloth substrates.

Experiments for the oxygen reduction reaction (ORR) was made in acid media, using a rotation ring-disk electrode (RRDE). Results have shown that NH₃ treated materials present superior electrocatalytic activity for the ORR and that the overall activity of Fe/NC(NH₃) is enhanced when large surface area carbon supports are employed for the catalyst preparation, in agreement with the increased content of N-C sites. Fractions of H₂O₂ detected in the ring RRDE are always small, showing that the reaction involves ca. 4 electrons per oxygen molecule, having water as the main product. XPS data indicate that the Fe/NC(NH₃) catalyst presents enhanced content of Fe-CN_x and N-C ORR active sites, as compared to Fe/NC(N₂), explaining its larger activity for the a ORR.

On the other hand, the carbon dioxide and the water reduction reactions were investigated in CO₂-saturated 0.1 M KHCO₃ solutions, under potentiodynamic and potentiostatic conditions, by on line differential electrochemical mass spectrometry (DEMS) and in line gas chromatography (GC). For all catalysts, an increase of the production of both, H₂ and CO, with the increase of the cathodic potential is observed, as indicated by DEMS and GC results. The Faradaic efficiency of CO formation for the NC(NH₃) and Fe/NC(NH₃) materials are substantially high, with that for the former being somewhat higher than for the later, in all applied potentials. The opposite occurs for the hydrogen Faradaic efficiency. Results for the NC(NH₃) electrocatalyst confirm that pyridinic-N groups (in absence of FeN₄ moieties) are active sites for promoting the CO₂RR to form CO with high selectivity, but at smaller rates as compared to Fe/NC(NH₃).

Agradecimentos:

CNPq, Fapesp e Capes

* e-mail do autor principal: edsont@iqsc.usp.br