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Promoting Carbon Monoxide Electrooxidation on Platinum and Rhodium by Adsorbed Sulfur

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Electrooxidation of carbon monoxide (CO) is an important process in methanol fuel cells (MFC). It is known that the self poisoning of Pt catalysts in MFC arises from reaction intermediate CO binding strongly to surface sites and therefore blocking methanol dissociation. Some metals, such as ruthenium or osmium, when present on Pt surfaces as islands or alloying with Pt, significantly improve the performance of MFC. The metal adatoms are believed to provide a facile reaction pathway to oxidize adsorbed CO. In this presentation, we will demonstrate a similar catalytic effect of adsorbed sulfur on the electrooxidation of CO on Pt and Rh in acdic solutions. This catalytic activity is in contrast to the common perception that Sads is a reaction poison. In contrast to Pt and Rh, CO oxidation is inhibited on S-covered Pd and Au. Surface-enhanced Raman (SER) spectra showed that the metal-S stretch (ν_{M-S}) frequency is higher for the former two metals than the latter. Based on the cyclic voltammogram and Raman results, a tentative reaction mechanism will be discussed.

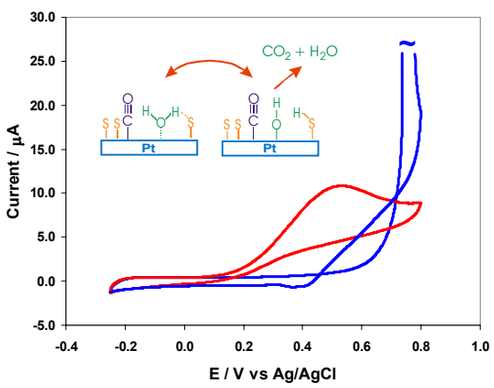

Fig. 1 Cyclic voltammogram of carbon monoxide oxidation on S-covered Pt electrode in CO-saturated 0.1 M $HClO_4$. Electrode geometric area: 0.03 cm^2; Scan rate: 100 mV/s.