

Platinum Systems Electrodeposited in the Presence of Iron or Palladium Concomitantly or not with Rutin or Quercetin on a Glassy Carbon Surface Effectively Catalyze Oxygen Reduction Reaction

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Introduction

One barrier to the dissemination of fuel cells is the complexity and irreversibility of the oxygen reduction reaction (ORR) in aqueous media, which impose a series of practical limitations, in addition to difficulties in obtaining information on the mechanism and kinetics of this phenomenon [1].

Platinum is the most active material and the main component in catalysts employed in fuel cells for low temperature operation [2]. Even with platinum catalysts, higher cathodic overpotentials in the range of 500-600 mV are required in order to achieve useful current densities in fuel cells, revealing the slow kinetics of ORR in acid solutions [3].

Electrodeposition is a practical method for generating a variety of Pt and Pt-based nanomaterials [4] and has been applied to grow metal nanostructures and multilayer metal thin films [4,5]. It has been reported as a method of choice, given its remarkable simplicity and low cost (low energy requirements and minimal material waste) for generating nanostructured materials [6].

The purposes of the present study were to perform direct electrodeposition of Pt and Pd catalysts (in the absence and presence of Fe, concomitantly or not with rutin or quercetin) and a Pt-Pd alloy on a glassy carbon (GC) surface; to investigate the electrochemical profiles of these catalysts using cyclic voltammetry (CV); and to investigate electrocatalytic activity (important electrocatalytic activity was found for some of the catalysts produced) and reaction mechanism in ORR using hydrodynamic cyclic voltammetry (HCV) with a rotating disk electrode. Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) microanalysis were employed to characterize the electrocatalysts.

Experimental

Voltammetric measurements, held in an AFCBP1 bipotentiostat coupled to an MSR speed controller, were conducted using a three-electrode glass cell with a working electrode consisting of a GC rotating disk (0.2 cm² in geometric area) properly polished and cleaned in 0.1M HClO₄ before each electrochemical experiment. The counter-electrode was a Pt plate. A reversible hydrogen electrode (RHE) served as the reference electrode. SEM was performed on a JEOL JSM-6380LV field-emission scanning electron microscope equipped with an EDX system (Thermo Noran System Six) to microanalyze Pt and Pd ratios in the electrodeposited nanoparticles.

H₂PtCl₆·6H₂O, FeSO₄·7H₂O, and PdCl₂ were the salts or precursor solutions used, in addition to rutin and quercetin. Electrode designations are based on molar concentration ratios of the metals employed—e.g., the electrode named Pt(0.50)/Pd(0.50)+rutin was obtained using Pt and Pd concentrations of 0.50 and 0.50 mM, respectively, resulting in a 1.00 mM concentration for the two-metal mixture in the presence of 0.1 mM rutin.

Results and Discussion

Figure 1 shows HCV curves for modified GC electrodes in an O₂-saturated 0.1 M HClO₄ solution.

Positive-going scans for modified GC surfaces revealed that O₂ reduction starts very close to maximum current densities—the region of diffusion-limiting current densities—which decrease at a potential coinciding with the beginning of the region related to Pt oxide formation (region of kinetic current densities). *E*_{1/2} was higher for the GC electrode modified with Pt(0.50)/Pd(0.50)+rutin and decreased by 30 mV after the stability test.

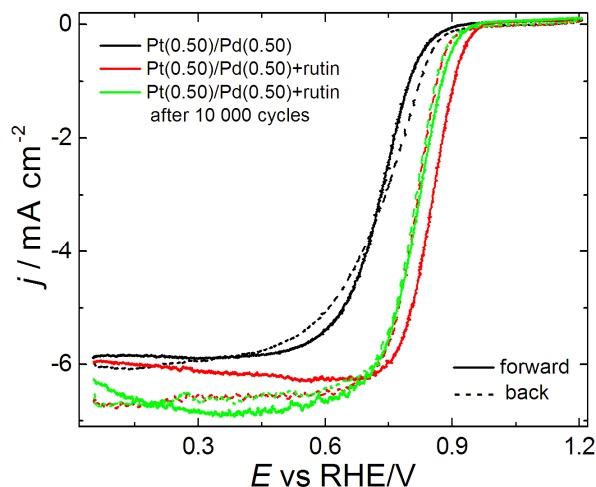


Figure 1: HCV curves for a GC disk electrode modified with Pt(0.50)/Pd(0.50) and for Pt(0.50)/Pd(0.50)+rutin (produced in presence of 0.1 mM rutin) before and after stability test (10 000 cycles between 0.6 and 1.0 V at 50 mV s⁻¹) in O₂-saturated 0.1 M HClO₄. $\omega = 1600$ rpm. $v = 10$ mV s⁻¹. Scans start at 0.05 V.

Conclusions

The results revealed the high catalytic activity toward ORR (in terms of specific activity (SA) ≈ 0.82 mA cm⁻², electrochemically active surface area (ECSA) ≈ 1.8 cm², and *E*_{1/2} ≈ 0.85 V) of the Pt(0.50)/Pd(0.50)+rutin catalyst (composed from Pt(0.50)/Pd(0.50)+rutin electrodeposited at an atomic ratio of 26:74, far from to the initial Pt:Pd atomic ratio of 73:27). After 10 000 cycles of potential sweep, however, ECSA was decreased to 1.0 cm² (a 45% loss, from 1.8 cm²). SA correction for an ECSA value of 1.0 cm² resulted in 0.55 mA cm⁻² at 0.85 V. Also, Tafel inclination values (close to -60 and -127 mV dec⁻¹ for low and high currents, respectively) and the number of transferred electrons (around 4.0) are suggestive of direct reduction of O₂ to water.

References

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