PLATINUM-BASED ELECTROCATALYSTS FOR GENERATION OF HYDROGEN PEROXIDE IN AQUEOUS ACIDIC ELECTROLYTES: ROTATING RING-DISK STUDIES

Yibo Mo and Daniel A. Scherson
Department of Chemistry
Case Western Reserve University
Cleveland, OH 44106-7078

INTRODUCTION

The reduction of dioxygen in aqueous electrolytes, including Nafion, has received extraordinary attention over the past few decades.[1] Much of the research impetus has been driven by the need to improve the performance of gas permeable cathodes for fuel cells applications, including stationary energy generation, vehicular propulsion, and, more recently, portable electronics. Yet another electrochemical process that involves O_2 as a reactant is the electrosynthesis of hydrogen peroxide, an environmentally benign chemical currently being considered for use in diverse technological areas, ranging from the industrial bleaching of paper[2] and wastewater treatment, to oxidation of hazardous chemicals and bioremediation. Although certain types of carbon are effective electrocatalysts for the 2 e^- reduction of O_2 in alkaline media, in terms of potency and high selectivity,[3] materials displaying equally desirable properties in acid electrolytes are quite rare. As will be shown, Pt surfaces modified by either Se or S display faradaic efficiencies for H_2O_2 generation (f) in acid media approaching 100% within a rather narrow range coverages.

EXPERIMENTAL

The methodologies involved in the preparation and electrochemical characterization of modified Pt electrodes were largely based on the reports of Wieckowski *et al.*[4,5] for S and Feliu *et al.*[6] for Se, and those of Stickney et al.[7,8] for S-, and Se-modified single crystal Au surfaces. Mechanistic studies aimed at assessing the activity ($\mathcal{A}$) and selectivity ($\mathcal{S}$) of Se- and S-modified polycrystalline Pt surfaces for O_2 reduction to H_2O_2 as a function of coverage were performed using a commercial Pt-Pt rotating disk electrode (Pine Instruments, collection efficiency 0.22.).

RESULTS AND DISCUSSION

Plots of i_{disk} (upper panel), i_{ring} (middle panel) and $|i_{ring}/i_{disk}|$ (lower panel) vs E_{disk} for a bare (curves a) and Se-modified Pt disk of a Pt/Pt RRDE electrode (curves b – f) in O_2-saturated 0.50 M H_2SO_4 at ω = 400 rpm for θ_{Se} = 0.15 (curves b), 0.25 (curves c), 0.34 (curves d), 0.51 (curves e), 1.24 (curves f) are shown in Fig. 1. Se coverages were calculated by subtracting the charge under oxidative stripping curves in the presence from those in the absence of Se on the surface assuming a 6-electron transfer for Se oxidation. Actual coverages were determined by normalizing these values using hydrogen adsorption from voltammetric curves recorded in the absence of Se. As can be inferred from these data, both the activity and specificity of the modified surface for peroxide generation are markedly influenced by the coverage of Se. These effects can be better visualized from plots of i_{lim} (solid circles, left ordinate) and $2i_{ring}$ /N (open circles, right ordinate) vs θ_{Se} based on the data shown in Fig. 1 at ω = 400 rpm (see caption for details). Based on these data, optimum values for activity and specificity for hydrogen peroxide generation are observed for Se coverages of ca. 0.5. In fact, conventional Levich plots obtained for Pt surfaces modified by half a monolayer of Se yielded a value for the slope precisely one half that found for the same electrode in strict absence of Se. Similar studies involving S modified Pt surfaces not shown in this work were also found o yield optimum activity and specificity for this process over a narrow range of coverages. Efforts are now underway to exploit the potential dependence of the Se coverage on Pt to prepare high area materials using an electrochemical fluidized bed reactor and thus test the performance of the catalyst under more technical conditions.

ACKNOWLEDGMENTS

This work was supported by a contract from CAMP.

REFERENCES

(1) Adzic, R. Recent advances in the kinetics of oxygen reduction. In *Electrocatalysis*; Lipkoswki, J., Ross, P. N., Eds.; Wiley-VCH, Inc.: New York, 1998; pp 197.
(2) Sethi, R. P.; Rao, B. K.; Srinivas, D. *Chem. Ind. Dig.* **2001**, *14*, 95.
(3) *Kinetics and Mechanisms of Electrode Precesses*; Tarasevich, M. R.; Sadkowski, A.; Yeager, E. B., Eds.; Plenum Press: New York, 1983; Vol. 7, pp 788.
(4) Sung, Y. E.; Chrzanowski, W.; Zolfaghari, A.; Jerkiewicz, G.; Wieckowski, A. *J. Am. Chem. Soc.* **1997**, *119*, 194.
(5) Sung, Y.-E.; Chrzanowski, W.; Wieckowski, A.; Zolfaghari, A.; Blais, S.; Jerkiewicz, G. *Electrochim. Acta* **1998**, *44*, 1019.
(6) Feliu, J. M.; Gomez, R.; Llorca, M. J.; Aldaz, A. *Surf. Sci.* **1993**, *289*, 152.
(7) Huang, B. M.; Lister, T. E.; Stickney, J. L. *Surf. Sci.* **1997**, *392*, 27.
(8) Lister, T. E.; Stickney, J. L. *J. Phys. Chem.* **1996**, *100*, 19568.

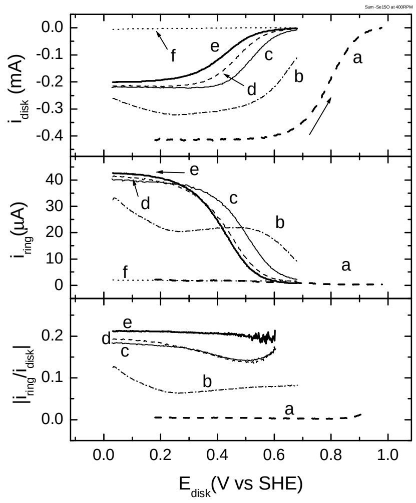

Figure 1. Plots of i_{disk} (upper panel), i_{ring} (middle panel) and $|i_{ring}/i_{disk}|$ (lower panel) vs E_{disk} for a bare (curves a) and Se-modified Pt disk of a Pt/Pt RRDE electrode (curves b – f) in O_2-saturated 0.50 M H_2SO_4 at ω = 400 rpm for θ_{Se} = 0.15 (curves b), 0.25 (curves c), 0.34 (curves d), 0.51 (curves e), 1.24 (curves f).

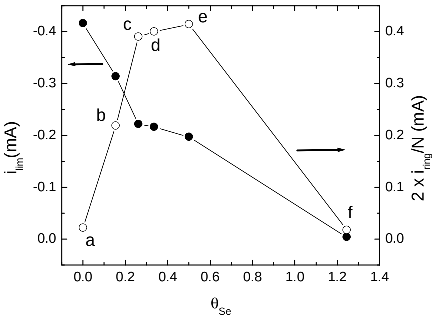

Figure 2. Plots of i_{lim} (solid circles, left ordinate) and $2i_{ring}$ /N (open circles, right ordinate) vs θ_{Se} based on the data shown in Fig. 4 at ω = 400 rpm (see caption for details). The collection efficiency based on the geometry of the RRDE assembly is 0.22.