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QUANTITATIVE CORRELATIONS BETWEEN THE COVERAGE AND THE NORMAL INCIDENCE DIFFERENTIAL REFLECTANCE FOR BROMIDE ADSORBED ON A POLYCRYSTALLINE PLATINUM ROTATING DISK ELECTRODE

Jing Xu and Daniel Scherson

Department of Chemistry, Case Western Reserve University, Cleveland, OH 44106

This work describes a technique that allows correlations to be obtained between the coverage of bromide as determined by the method of Gasteiger et al.[1] and the normal incidence reflectance signal on a polycrystalline Pt disk of a Pt|Pt electrode rotating ring disk electrode, RRDE. Shown in Fig. 1 are plots of I_{ring} vs E_{disk} for E_{disk} scanned toward negative potentials for 10^{-5}M KBr (red) or 10^{-4}M KBr (blue) in 0.1 M $HClO_4$, at ν = 10 mV/s and a rotation rate, ω = 900 rpm. As discussed by Gasteiger et al.[1], the integral of I_{ring} provides a measure of the absolute amount of adsorbed (or desorbed) Br^- on the disk electrode as a function of E_{disk}, which serves as a basis for determining precise adsorption isotherms. These are displayed in smooth solid lines in Fig. 1, where the bromide coverage was normalized by its saturation value to account for slight differences in the areas of the peaks (up to 6%) derived from differences in surface roughness.

Addition of Br^- elicits changes in the optical response of the interface due to modifications in the electronic properties of the metal surface induced by adsorption of the halide. This effect is illustrated by plots of of$-\Delta R/R = -[R(E_{ref}) - R(E_{sam})]/R(E_{ref})$ vs E_{disk} recorded under the same conditions specified in the caption, Fig. 1, during the scan in the negative direction in 0.1 M $HClO_4$ before (black curve) and after addition of 10^{-5} M KBr (red) (see Fig. 2). As is customary, $R(E_{ref})$ and $R(E_{sam})$ are the reflectance values recorded at the reference potential, E_{ref}, set at 0.05 V in our case, and at any arbitrary sampling potential, E_{sam}, respectively. The optical signals could be modeled by assuming the normalized reflectance could be ascribed to areas covered hydrogen and by bromide, i.e.

$$-\Delta R/R = \beta(E)\times(1-\theta_{Br^-}) + (\theta_{Br^-}/\theta_{Br^-}^{sat})\times f(E)$$

where $\beta(E)$ (blue) and *f(E)* (olive) represent the potential dependence of the two types of areas (see Fig. 2) Strong evidence for the validity of this model was obtained by overlaying on the same graph both $-\Delta R/R$ vs E_{disk} and the function on the right hand side of Eq. above based on the data in Fig. 2 (see Panel A, Fig. 3), and the corresponding data for 10^{-4}M KBr (see Panel B in the same figure). These are shown in black and blue symbols in Panels A and B, respectively.

Applications, now under development in our laboratory, will enable for the coverage of bromide and, in principle, other species capable of undergoing specific adsorption to be monitored while a faradaic reaction is taking place under well-defined mass transport control.

REFERENCES

1. Gasteiger, H. A.; Marković, N. M.; Ross, P. N., *Langmuir* **1996,** *12* (6), 1414-1418.

ACKNOWLEDGEMENTS

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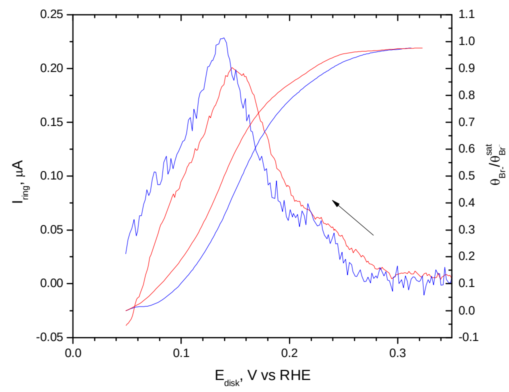

Fig. 1. Plot of I_{ring} vs E_{disk}, for E_{disk} scanned toward negative potentials (see arrow) for 10^{-5}M KBr (red) or 10-4M KBr (blue) in 0.1 M $HClO_4$, during a linear scan at ν = 10 mV/s, and ω = 900 rpm. The smooth red and blue lines represent the corresponding normalized bromide isotherms, i.e. coverage, $\theta_{Br^-}/\theta_{Br^-}^{sat}$ (right ordinate) as a function of E_{disk} obtained by integrating I_{ring}.

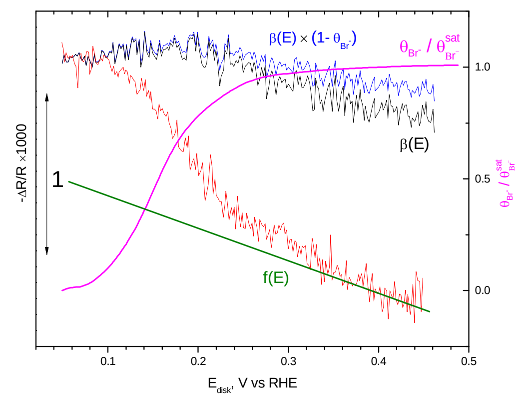

Fig. 2. Plots of $-\Delta R/R$ vs. E_{disk} 0.1 M $HClO_4$ before (*β(E)*, black), and after addition KBr to reach 10^{-5}M recorded under the conditions specified in the caption, Fig. 1. Also shown in this figure are plots of $\beta(E)\times(1-\theta_{Br^-})$ (blue) and *f(E)* (olive) vs E_{disk} (see text) for a solution containing 10^{-5}M KBr. The smooth magenta line represents the corresponding normalized bromide isotherm, i.e. $\theta_{Br^-}/\theta_{Br^-}^{sat}$ vs. E_{disk} (right ordinate).

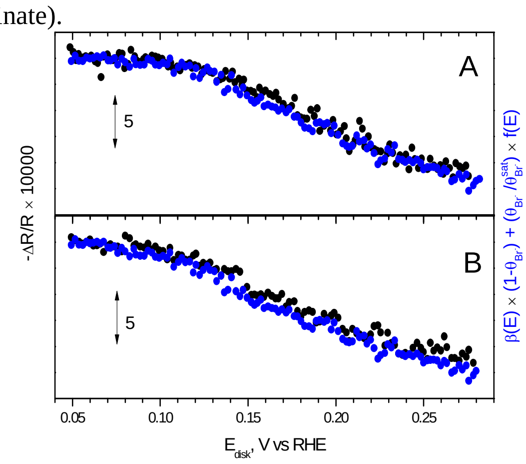

Fig. 3. Plots of $-\Delta R/R$ vs E_{disk} (black symbols) and the function on the right hand side of Eq.(1) (blue symbols) based on the data in Fig. 2 for 10^{-5}M KBr (see Panel A), and for the corresponding data for 10^{-4}M KBr (Panel B).