Illumination-Dependent Electrochemical Impedance Analysis of Bi_2O_3-Based photoelectrodes

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Bismuth oxide (Bi_2O_3) has attracted considerable attention as a multifunctional material for electrochemical energy storage and optoelectronic applications due to its favorable redox activity, semiconducting properties, and tunable morphology [1]. Despite these advances, the influence of substrate, interfacial properties, and external factors such as applied potential and illumination on the electrochemical behavior of Bi_2O_3 thin films remains insufficiently explored. This paper presents the results of EIS analysis of Bi_2O_3-based thin films.

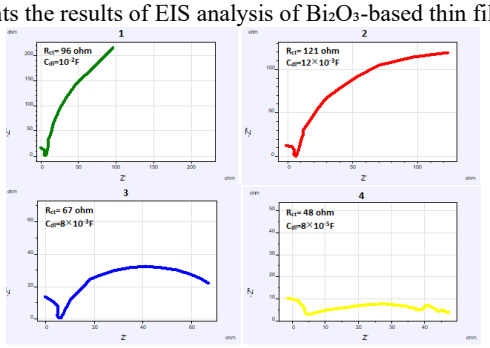


Figure 1. Nyquist impedance spectra for the Ni/Bi_2O_3 electrode in 0.5 M Na_2SO_4 solution at various potentials. (1) −0.4 V (2) −1.15 V; (3) −1.25 V; (4) −1.5 V.

The electrochemical impedance spectroscopy (EIS) results of the Ni/Bi_2O_3 electrode in 0.5 M Na_2SO_4 at different applied potentials are presented as Nyquist plots in Fig. 1. Each spectrum exhibits a depressed semicircle in the high-to-medium frequency region followed by a low-frequency tail, indicating the coexistence of charge transfer and diffusion-controlled processes. The diameter of the semicircle, corresponding to the charge transfer resistance (Rct), shows a strong dependence on the applied potential. At **−0.4 V,** a relatively large semicircle (Rct ≈ 96 Ω) is observed, suggesting sluggish electron transfer kinetics and limited electrochemical activity. As the potential shifts to −1.15 V, the Rct increases further (≈121 Ω), which may be attributed to the adsorption of reaction intermediates or partial blockage of active sites on the electrode surface. Upon increasing the cathodic potential to −1.25 V, the Rct decreases significantly (≈67 Ω), indicating enhanced charge transfer and improved reaction kinetics. At −1.5 V, the smallest semicircle is obtained (Rct ≈ 48 Ω), reflecting highly facilitated electron transfer and increased electrocatalytic activity. Additionally, the more pronounced low-frequency tail at higher overpotentials suggests that diffusion processes become dominant. Overall, these results demonstrate that increasing the cathodic potential activates the electrode surface and promotes faster electrochemical reactions, likely associated with reduction processes such as hydrogen evolution.

The decrease in Rct with increasing negative potential confirms the enhanced electrocatalytic activity of the Ni/Bi_2O_3 electrode.

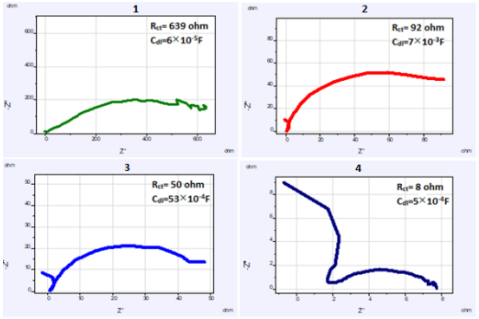


Figure 2. Nyquist impedance spectra for the Ni/Bi2O3 electrode in 0.5 M Na2SO4 solution at various potentials were carried out under illumination. (1) −0.4 V (2) −1.15 V; (3) −1.25 V; (4) −1.35 V.

The corresponding charge (Rct) and double-layer capacitance (Cdl) values were obtained by fitting the experimental data using an equivalent circuit model. A significant decrease in R_ct is observed with increasing cathodic potential, indicating enhanced charge transfer kinetics at more negative potentials. Specifically, Rct decreases from 639 Ω at −0.40 V to 8 Ω at −1.35 V, suggesting improved electrochemical activity of the Ni/Bi_2O_3 electrode under illumination. Meanwhile, the variation in Cdl reflects changes in the electrochemically active surface area and interfacial properties.

The combined effect of illumination and applied potential significantly enhances the interfacial charge transfer kinetics, highlighting the potential of the Ni/Bi_2O_3 system for photoelectrochemical applications.

References

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