

Investigation of potential oscillations during the electro-oxidation of urea on Ni catalyst in alkaline medium

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Recently, electrolysis of urea-rich wastewater has gained much attention due to its ability to produce hydrogen as alternative fuel, while cleaning the wastewater¹⁻³. At the anode, urea is electrochemically oxidized to nitrogen (N₂) and carbon dioxide (CO₂), whereas water is reduced to hydrogen (H₂) at the cathode. Boggs et al.¹ demonstrated that urea can be electrochemically oxidized on a transition-metal catalyst, nickel (Ni), in alkaline medium. The underlying reaction mechanism has not been completely understood or studied extensively. Recently we reported that electrocatalytic oxidation of urea on Ni catalyst follows a catalyst regeneration mechanism⁴.

Electrochemical oscillations are well known to occur during the electrocatalytic oxidation of small organic molecules at the surfaces of Pt and Pt group metals^{5, 6}. The electrochemical oscillations during the methanol oxidation at Pt electrodes have been related to the autocatalytic reaction where the adsorbed CO is oxidized to CO₂⁷. For the first time, potential oscillations have been noticed during the electrocatalytic oxidation of urea on Ni catalyst in alkaline medium. Deciphering the cause for the potential oscillation during the electrochemical oxidation of urea will aid in understanding and proposing a realistic mechanism for urea oxidation reaction on Ni catalyst in alkaline medium.

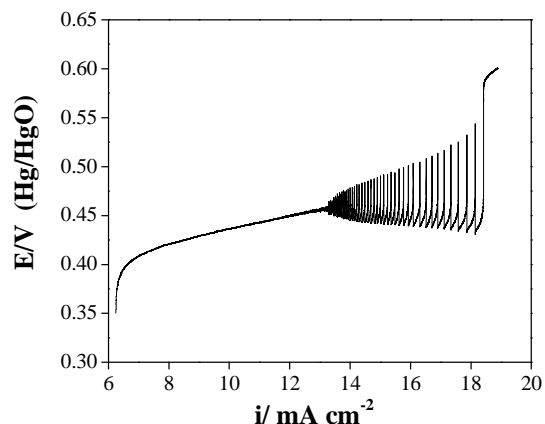


Fig. 1 Galvanodynamic curve for the electrochemical oxidation of urea on Ni using 0.25 M urea + 5 M KOH solution. Scan rate: 0.001 mA/s.

The potential oscillation experiments were conducted using Ni foil, Pt foil, and Hg/HgO as working, counter, and reference electrodes, respectively. Galvanodynamic experiment was carried out in 0.25 M urea + 5 M KOH solution at a scan rate of 0.001 mA/s (Fig. 1). The data suggest that potential oscillations are possible during the electro-oxidation of urea on Ni catalyst. The galvanodynamic curve was overlapped on the cyclic voltammogram for Ni obtained with 0.25 M urea + 5 M KOH solution (10 mV/s) and the result is shown in Figure 2. The plot shows that the potential oscillations occur at the urea oxidation region observed in

the cyclic voltammogram. This confirms that the potential oscillations are related to the electro-oxidation of urea molecules. But the exact phenomenon to instigate the oscillation of potential needs to be investigated.

The objective of the study is to understand the underlying mechanism during the potential oscillation of electro-oxidation of urea on Ni catalyst. Various electrochemical techniques such as cyclic voltammetry, galvanodynamic, and galvanostatic experiments will be employed. Electrochemical coupled Fourier Transform Infrared Spectroscopy (FTIR) will also be used to understand the potential oscillations.

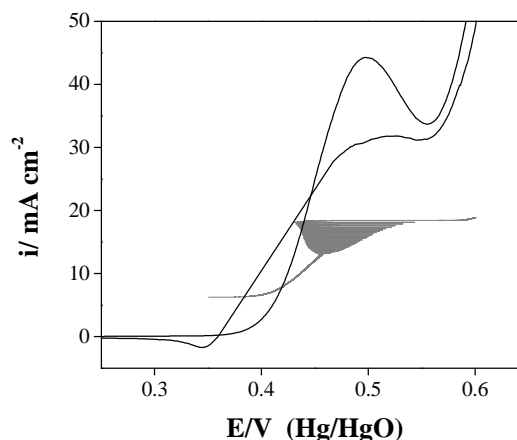


Fig. 2 Cyclic voltammogram for Ni in 0.25 M urea + 5 M KOH solution at a scan rate of 10 mV/s. The galvanodynamic curve from Fig. 1 is overlapped with the cyclic voltammogram.

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