

Assessing Charge and Mass Balance over time in Urea Electrooxidation Reaction on Nickel Modified Electrodes with Fourier Transform Infrared Spectroscopy

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Highlights

- Ni_{0.8}M_{0.2}/NF electrodes were prepared for long time electrooxidation of urea.
- Solution concentration was monitored using FTIR spectroscopy.
- Separated and non-separated compartments were used.
- The reduction in concentration of OH⁻ species led to a decrease in reaction rate for both cases.

1. Introduction

With the growing global emphasis on the urgent need for an energy transition towards sustainable and environmentally friendly solutions, electrochemical processes for hydrogen (H₂) production have attracted considerable attention. Among these processes, the electrooxidation of urea represents a promising avenue for clean energy production[1]. To fully understand urea electrooxidation reaction mechanism and kinetics is important to follow changes in solution medium over the reaction time. In this study, FTIR spectroscopy was used to monitor the chemical reactions during time for bimetallic nickel based modified electrodes in separated and non-separated compartments.

2. Materials and Methods

Synthesis of modified electrodes and characterization

Nickel foam modified electrodes were prepared by a simple one-step hydrothermal method. The modification involved the incorporation of Ni_{0.8}M_{0.2} nanoparticles into the support surface, where M = Rh, Cu, Co and Mo.

The size, shape and distribution of the nanoparticles were observed by scanning electron microscopy (SEM). Cyclic and linear sweep voltammetry were used to investigate the electrochemical behavior of the modified electrodes in our system. The effective electrochemical surface area (ECSA) was estimated by measuring the Double Layer Capacitance (C_{dl}) and then dividing it by the Specific Capacitance (C_s).

Electrolysis

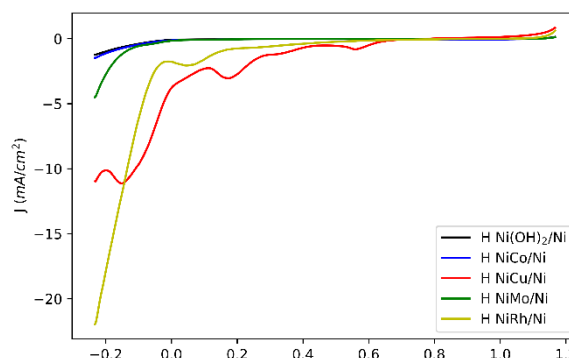
Electrolysis experiments were carried out in an H-type reactor. Fourier Transform Infrared Spectroscopy (FTIR) was used to monitor changes in chemical composition during the electrochemical processes. The anolyte consisted in a solution of urea at 0.5 M and 1 M KOH solution while catholyte consisted of a 1 M KOH solution.

3. Results and discussion

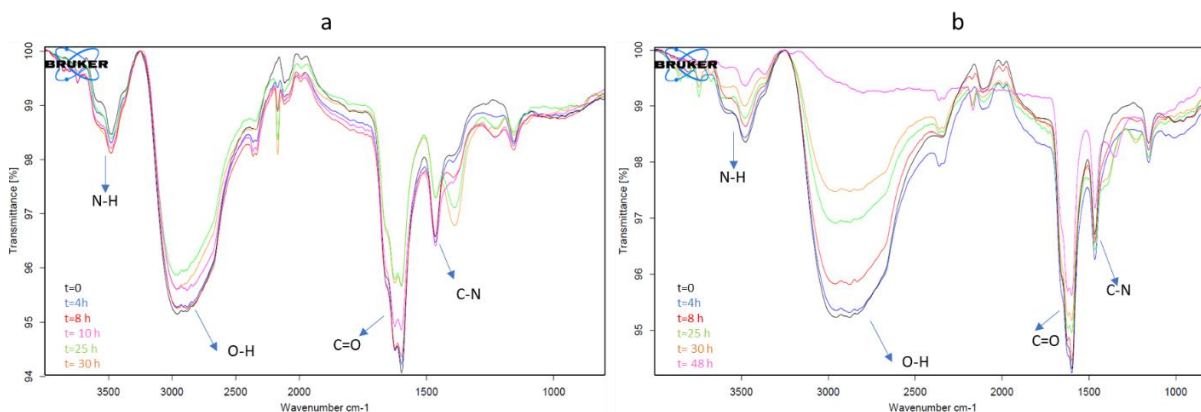
The successful construction of Ni_{0.8}M_{0.2}/NF modified electrodes was achieved by a single step hydrothermal reaction. Table 1 shows the double layer capacitance values for these electrodes, providing insight into their electrochemical characteristics. Notably, Ni_{0.8}Rh_{0.2}/NF on nickel foam exhibited the lowest onset potential and the smallest Tafel slopes for the Hydrogen Evolution Reaction (HER) (Fig. 1), indicating its superior electrocatalytic activity compared to other electrode compositions.

Table 1. Cdl of modified electrodes

Support	Cat.	C _{dl} μFg ⁻¹
Nickel	Ni	32.0
	Ni _{0.8} Co _{0.2}	44.0
	Ni _{0.8} Cu _{0.2}	42.5
	Ni _{0.8} Mo _{0.2}	23.0
	Ni _{0.8} Rh _{0.2}	175.5

**Figure 1.** Polarization curves of modified nickel foam electrodes in KOH 1 M.

In Figure 2, the Fourier Transform Infrared Spectroscopy (FTIR) spectrum provides a visual representation of the reaction medium at different time of electrolysis at 1500 mV vs. RHE. In general, spectrums show a notable change in chemical composition. For a not separated compartments Fig.2a an unexpected O-H reduction is observed, probably due to electrode corrosion forming $Ni(OH)_2$ at the cathode. Two new peaks were observed, at 2200 cm⁻¹ and 1300 cm⁻¹. For the proton exchange separated compartments experiments, a fast reduction in OH⁻ peak is observed due to NiOOH formation at the anode prior to urea oxidation reaction to CO₂ and N₂. After 48 h of reaction, OH⁻ peak was not more detected in the FTIR spectrum, and not more current was measured by the potentiostat, indicating the cessation of the urea electrooxidation reaction due to the lack of OH⁻ species in the medium.

**Figure 2.** FTIR spectrums at different reactions time for a) non-separated compartments and b) compartments separated by a proton exchange membrane.

4. Conclusions

FTIR spectroscopy was employed to monitor the urea electrooxidation reaction in both separated and non-separated compartments. These findings offer insights crucial for the design of an enhanced electrochemical reactor, contributing to the advancement of green hydrogen production.

Reference

- [1] V. Vedharathinam and G. G. Botte, "Understanding the electro-catalytic oxidation mechanism of urea on nickel electrodes in alkaline medium," *Electrochim. Acta*, vol. 81, pp. 292–300, 2012, doi: 10.1016/j.electacta.2012.07.007.

Keywords

Green hydrogen production; Nickel modified electrodes; FTIR spectroscopy; Reaction Kinetics.