Cobalt-nickel composite nano-grass as an excellent electrode for urea oxidation

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Mechanism of urea oxidation over Cobalt-based catalyst:

Recently, researchers have concentrated on overcoming nickel's essential limitations as an electrocatalyst. This has been accomplished by alloying nickel with additive catalysts or discovering novel potential catalysts capable of oxidizing urea at low potentials while retaining excellent electrocatalytic activity. Cobalt and cobalt oxide-based materials are very appealing for electrochemical applications [1]. including oxygen reduction reactions [2], electrochemical sensors [3], energy storage [4], methanol oxidation [5], or nitrite oxidation [6].

According to Equation (1), in alkaline media, urea combines with OH^- to produce water, nitrogen, carbon dioxide, and electrons at the anode of DUFC "direct urea fuel cell". These electrons are transferred to the cathode side, where they react with oxygen and water, producing OH^- as seen in Equation (2). These hydroxyl ions are transferred through the anion exchange membrane from the cathode to the anode. Equation (3) shows the overall cell reaction of urea into carbon dioxide, nitrogen, and water, while producing electricity [7].

According to Equation (1), six electrons must be transferred for this process to occur (complete oxidation of the urea fuel at the anode). Two electrons are needed for the oxidation of the CO, four electrons are needed for the dehydrogenation of the N-H bonds, and N-N coupling that does not involve electron transfer. Understanding the urea oxidation reaction's (UOR) microscopic route is essential to the purposeful design of catalysts that would improve the activity of the electrocatalytic reaction.

Anodic reaction

$$CO(NH_2)_2 + 6OH^- \rightarrow CO_2 + N_2 + 5H_2O + 6e^- \qquad E_{anode} = -0.746\ vs.\ SHE \qquad (1)$$

Cathodic reaction

$$^3/_2 O_2 + 3H_2O + 6e^- \rightarrow 6OH^- \qquad E_{cathode} = 0.401\ vs.\ SHE \qquad (2)$$

Overall cell reaction

$$CO(NH_2)_2 + {}^3/_2 O_2 \rightarrow CO_2 + N_2 + 2H_2O \qquad E_{cell} = 1.147\ V \quad (3)$$

$NiOOH/Ni(OH)_2$ is the active site that formed when nickel or nickel oxide is inserted in an alkali, Equation 4[8]:

$$Ni + 2OH^-(aq) \rightarrow Ni(OH)_2 + 2e^- \quad (4)$$

While performing the activation process (Cyclic voltammetry at 0.05 Vs^{-1} for 100 cycles in urea free KOH solution), the nickel hydroxide is converted into nickel oxy-hydroxide (NiOOH), Equation 5:

$$Ni(OH)_2 + OH^-(aq) \rightarrow NiOOH + H_2O + e^- \quad (5)$$

In the case of bare NF, $NiOOH/Ni(OH)_2$ is taking part as the main active site, while it took place in the activity of the Co/NF as Nickel exists in the NF support of the Cobalt hydroxide catalyst (Co/NF).

The formation of the $CoOOH/Co(OH)_2$, which is considered as an active site for the urea oxidation [9, 10] can be described in a similar way to the formation of the $NiOOH/Ni(OH)_2$ in alkaline media [11-14]. In alkaline media, the cobalt metal or its oxides is converted into the hydroxide form according to Equation 6:

$$Co + 2OH^-(aq) \rightarrow Co(OH)_2 + 2e^- \quad (6)$$

While performing the activation process, the cobalt hydroxide is converted into cobalt oxy-hydroxide (CoOOH), Equation 7:

$$Co(OH)_2 + OH^-(aq) \rightarrow CoOOH ++ H_2O + e^- \quad (7)$$

Cobalt catalyst enhances the adsorption and dehydrogenation of urea [1], Equation 8:

$$6CoOOH(s) + CO(NH_2)_2(aq) + 2OH^-(aq) \leftrightarrow CO^{2-}_3(aq) + 6Co(OH)_2(s) + N_2(g) \quad (8)$$

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