Nickel-cerium alloys for borohydride oxidation

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Sodium borohydride ($NaBH_4$) is being actively investigated in the last decade as an anodic fuel for direct borohydride fuel cells (DBFCs) [1]. The main reasons for that is because the solid state $NaBH_4$ is chemically stable and can be easily stored and distributed, the oxidation product, sodium metaborate ($NaBO_2$) is non-toxic and can be recycled back to $NaBH_4$, and there are no gaseous pollutants exhausted from the cell reactions. Moreover, the DBFC presents higher energy density than the direct methanol fuel cell.

Noble metal electrodes, namely gold (Au) and its alloys, display a rather good borohydride oxidation activity but their high cost makes them unsuitable for widespread applications [2]. Au promotes complete BH_4^- oxidation with 8 electrons exchanged (Eq. 1).

$$BH_4^- + 8\ OH^- \rightarrow BO_2^- + 6\ H_2O + 8\ e^- \quad (1)$$

However, most electrode substrates also promote the competitive BH_4^- hydrolysis reaction (Eq. 2) that reduces the overall coulombic efficiency of the process.

$$BH_4^- + 2\ H_2O \rightarrow BO_2^- + 4\ H_2 \quad (2)$$

For instance, nickel (Ni) electrodes present reasonable activity for BH_4^- oxidation but their simultaneous catalytic effect towards the BH_4^- hydrolysis leads to an overall number of exchanged electrons in the oxidation process between 2 and 4, instead of desirable value of 8 [3].

It has been recently shown that presence of rare earth (RE) elements in intermetallic alloy electrodes changes the electrode's activity for BH_4^- oxidation and hydrolysis and consequently alters reaction mechanism and main kinetic parameters [4]. Among other factors, these changes will depend on the composition of the alloying elements as well as on the applied anodic potential range.

In this paper, Ni and Ni-cerium (Ce) intermetallic alloy electrodes with different amounts of Ce (5 and 10 at.% Ce) are studied for BH_4^- oxidation in alkaline media by cyclic voltammetry (CV), chronopotentiometry (CP), and chronoamperometry (CA), in the temperature range 25 - 55 ºC.

Electrochemical data are modeled to obtain relevant kinetic parameters of BH_4^- oxidation at these electrodes, such as number of exchanged electrons, anodic charge transfer coefficient, and standard rate constant. Effect of electrolyte composition and temperature on the evaluated parameters has been investigated as well. Arrhenius plots are used to estimate the activation energies.

References

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