Hydrazine sensor for quantitative determination of high hydrazine concentrations for direct hydrazine fuel cell vehicle applications

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With the discovery of hydrazine as an alternative to hydrogen fuel for the development of fuel cell electric vehicles (FCEV), the need for a hydrazine sensor for the quantitative determination of hydrazine aroused. In contrast to the common hydrazine electrochemical sensors whose main parameters are the low detection and quantification limits, the new electrochemical sensor should satisfy one main requirement: a linear response at high hydrazine concentrations (2-4M hydrazine). This requirement is imposed by the fact that the sensor will be used for quantification and control of the hydrazine level in direct hydrazine fuel cells for vehicle applications. Daihatsu Motor Co., Ltd. has successfully developed a Pt-free direct hydrazine fuel cell with an anion-exchange polymer electrolyte, which was tested in a FCEV prototype. This fuel cell generates a maximum power of $0.5 \ W \ cm^{-2}$ (1250 mA cm^{-2} at 0.4 V) which is comparable to hydrogen polymer electrolyte fuel cells and exceeds the performance of direct methanol fuel cells[1].

In this study, three types of catalysts were tested for the oxidation of hydrazine and its electrochemical quantitative determination: $Ni_{0.87}Zn_{0.13}$, $Ni_{0.95}La_{0.05}$ and $Ni_{0.85}La_{0.15}$. The catalytic activity of these bimetallic catalytic systems for hydrazine oxidation in alkaline media has already been characterized[2]. In order to investigate the electrochemical response of N_2H_4 on such electrodes, cyclic voltammetry was utilized (Fig. 1).

Figure 1 shows noticeable increase of the oxidation currents proportional to the amount of hydrazine present in the system.
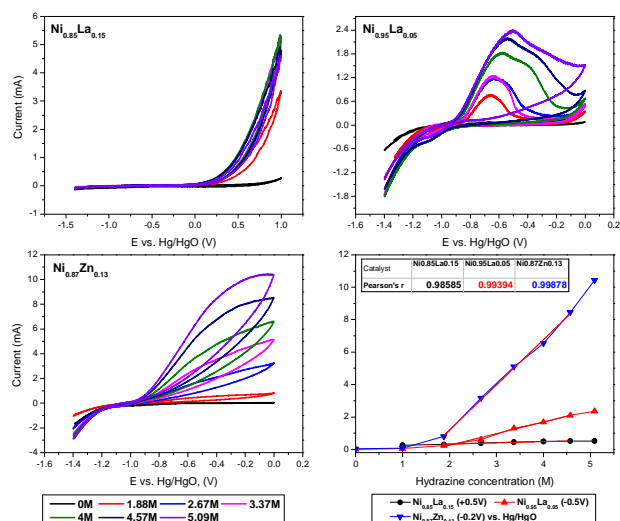

Figure 1: CVs of the three bimetallic catalysts in 1M KOH at different hydrazine concentrations (200 mV/s). Dependence of the current from hydrazine concentration.

When the amperometric response of the system at a defined potential was investigated, the expected linear dependence between the generated current and the hydrazine concentration was only valid for low hydrazine concentrations due to the high activity of the catalysts (Fig. 2). Therefore, the utilization of a diffusion control layer (DCL) to create diffusional limitations and expand the linear range of the electrochemical response was employed.
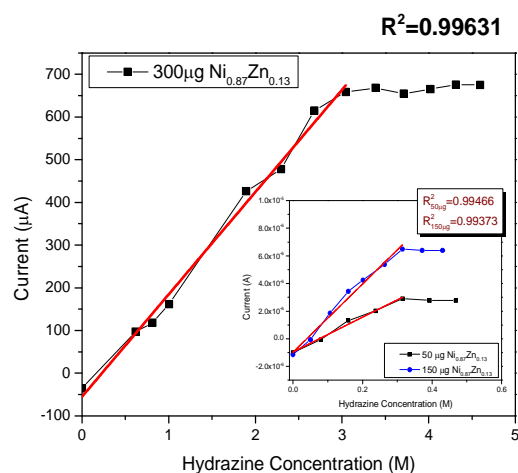

Figure 2: Plot of chronoamperometric currents as a function of hydrazine concentration for $Ni_{0.87}Zn_{0.13}$ catalyst at three catalyst loadings.

Catalysts-ionomer composites with layered structures were developed. Chronoamperometry measurements at -0.5 V vs. Hg/HgO with stepwise addition of hydrazine were carried out in order to create current/hydrazine concentration dependences (Fig. 3).
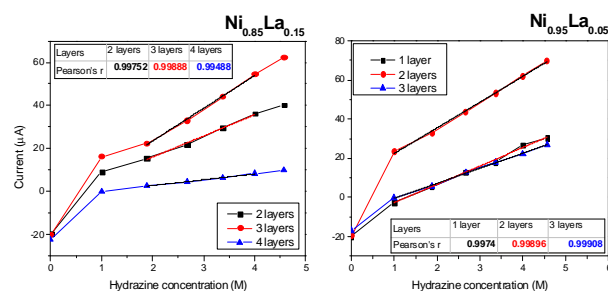

Figure 3: Plot of chronoamperometric currents as a function of hydrazine concentration for $Ni_{1-x}La_x$-DCL catalyst-ionomer composites.

Figure 3 shows that both $Ni_{1-x}La_x$-DCL composites produce a linear response within the necessary range with the highest sensitivity observed from the bilayer $Ni_{0.95}La_{0.05}$-DCL electrodes (13.2 µA M^{-1} N_2H_4 or 52.5 µA M^{-1} cm^{-2} N_2H_4). The increase of the number of layers led to an increase in the sensor selectivity to a defined magnitude after which, due to hindered conductivity and diffusional limitations, a decrease of performance was recorded. For each addition of hydrazine, the steady state currents rose and reached the stable value within less than 20 s, indicating that these electrodes have reasonably short response time for hydrazine detection.

Layer composites based on the utilization of $Ni_{1-x}La_x$ catalyst can be successfully explored in the development of hydrazine sensors for quantitative determination of high hydrazine concentrations towards direct hydrazine fuel cell vehicle applications.

(1) Asazawa, K., Yamada , K., Tanaka, H., Oka, A., Masatoshi Taniguchi, M., Kobayashi, T. *Angew. Chem. Int. Ed.* **2007**, *46*, 8024.
(2) Martinez, U., Asazawa, K., Halevi, B., Falase, A., Kiefer, B., Serov, A., Padilla, M., Olson, T., Datye, A., Tanaka, H., Atanassov, P. *Phys. Chem. Chem. Phys.* **2012**, *14*, 5512.