

Combinatorial discovery of Ni-based binary and ternary catalysts for hydrazine electrooxidation for use in anion exchange membrane fuel cells

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Direct methanol fuel cells (DMFCs) have been under intensive research for portable electronics applications such as mobile phones, mp3 players and notebooks within the last 20 years. However, to become commercially viable DMFCs have to overcome cost and availability barriers caused by the reliance on Pt and Pt-based catalysts in both anode and cathode electrodes. Direct hydrazine hydrate fuel cells (DHFCs) have been studied since the 1960s. Therefore hydrazine electro-oxidation electrodes and reaction mechanism have been under intensive study until today. Alloying Ni anodes has been shown to improve hydrazine oxidation efficiently though different alloying effects. These improved performance levels have motivated us to further study Ni-based binary and ternary catalysts for use in DHFCs. In this combinatorial study, carbon supported binary Ni-M (with M = Mn, Fe, Zn, La) and ternary Ni-Mn-Fe and Ni-Zn-La catalysts were synthesized using an impregnation/freezing-drying procedure. The catalytic activity of all prepared 79 samples was evaluated for hydrazine oxidation in alkaline media using a temperature controlled (4×4) 16-channel electrochemical combinatorial array for rapid parallel screening.

The linear sweep voltammetric (LSV) profiles of the Ni-Zn binary catalyst library are shown in Fig. 1. The catalytic activity for hydrazine oxidation was evaluated from -0.129 V to 0.221 V vs. RHE in 1 M KOH + 1 M hydrazine hydrate electrolyte at 60 °C. The onset potential is defined as the potential at 10.9 A·g⁻¹, and the mass activity is defined as the current per unit of total metal weight at 0.221 V vs. RHE. The anodic sweep in the potential range from 0 V to 0.221 V vs. RHE is ascribed to hydrazine oxidation as shown in Fig. 1. The inset figure shows the onset potentials of each catalyst for hydrazine oxidation. Zn/C has no catalytic activity for hydrazine oxidation in this potential range. In parallel, the catalytic activity of Ni/C for hydrazine oxidation is improved by the addition of Zn as shown in Fig. 1. Ni_{0.4}Zn_{0.6}/C was the best performing catalyst sample from the Ni-Zn binary library. The onset potential of the Ni_{0.4}Zn_{0.6}/C binary catalyst is also shifted toward lower potential when compared with that in Ni/C. Moreover, the onset potential of Ni_{0.8}Zn_{0.2}/C is significantly shifted in comparison with the Ni/C case as shown in the inset figure 1. The reduced

overpotential indicates improved catalyst intrinsic performance towards hydrazine electrooxidation and therefore indicates an single active alloyed phase rather than a multifunctional catalyst system. In contrast, the good activity for NiLa, also identified as a good candidate catalyst, is most likely due to synergistic effects in a multi-phase catalyst system.

From the results obtained from combinatorial binary catalyst study and our previous research, unsupported Ni_{0.87}Zn_{0.13} and Ni_{0.9}La_{0.1} catalysts were synthesized by spray pyrolysis and tested as anode catalysts for DHFCs. Fig. 2 shows the cell performances of DHFCs using unsupported Ni_{0.87}Zn_{0.13} and Ni_{0.9}La_{0.1} as an anode catalyst, together with conventional Ni catalyst (210H, INCO) as a reference catalyst. Co-PPY-C (PPY: polypyrrole) was used as a cathode catalyst. The DHFCs showed high performance without precious metal catalysts on either anode or cathode. When Ni, Ni_{0.87}Zn_{0.13}, or Ni_{0.9}La_{0.1} were used as an anode catalyst in DHFCs, the open circuit voltages (OCV) were observed 0.750 V, 0.777 V, and 0.758 V, respectively. The difference in observed OCV between Ni_{0.87}Zn_{0.13}, Ni_{0.9}La_{0.1}, and Ni relate to the improved onset potential for hydrazine oxidation when Zn (or La) is added to Ni. The maximum power density for Ni_{0.87}Zn_{0.13} and Ni_{0.9}La_{0.1}, 489 mW·cm⁻² and 462 mW·cm⁻², are 19% and 12% higher than the 411 mW·cm⁻² obtained for the pure Ni catalyst case, respectively. The improved performance of the unsupported Ni_{0.87}Zn_{0.13} and Ni_{0.9}La_{0.1} catalysts when compared to the Ni confirms the results of the carbon supported Ni_{1-x}Zn_x and Ni_{1-x}La_x (0.1 ≤ x ≤ 0.9) catalysts where the Ni_{0.8}Zn_{0.2}/C and Ni_{0.9}La_{0.1}/C formulation were the best performing anode catalyst in the Ni-based binary system for DHFCs.

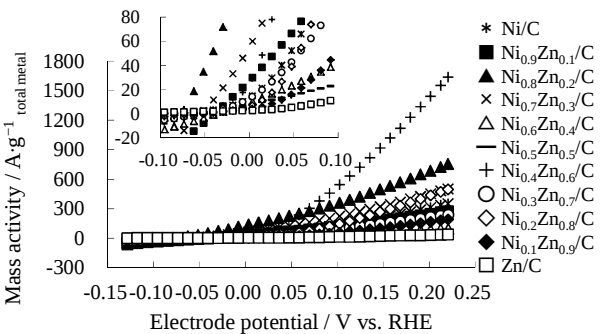


Fig. 1. LSV profiles of carbon supported Ni-Zn binary catalysts at scanning rate of 20 mV·s⁻¹.

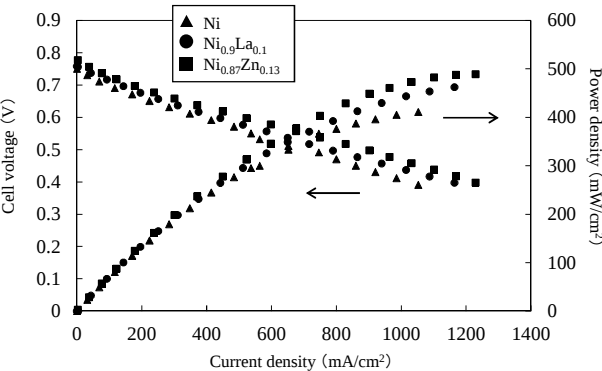


Fig. 2. Cell performances of unsupported Ni, Ni_{0.9}La_{0.1} and Ni_{0.87}Zn_{0.13} as an anode catalyst of DHFCs.

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