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Electrooxidation of hydrazine hydrate using Ni–La catalyst for anion exchange membrane fuel cells

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HIGHLIGHTS

- ► Ni–La/C catalysts were synthesized and investigated for hydrazine oxidation.
- ► The $Ni_{0.9}La_{0.1}/C$ catalyst exhibited the best onset potential and mass activity.
- ► HVEM suggested the metal particles are composed of Ni cores with Ni_xLa_y shells.

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ABSTRACT

Carbon supported Ni, La, and $Ni_{1-x}La_x$ ($0.1 \leq x \leq 0.9$) catalysts were synthesized by an impregnation/freeze-drying procedure followed by thermal annealing. The catalytic activity for electro-oxidation of hydrazine hydrate on anionic ionomer-coated catalysts was evaluated using a (4 × 4) 16-channel electrochemical electrode array in 1.0 M KOH + 1.0 M hydrazine hydrate solution at 60 °C. The $Ni_{0.9}La_{0.1}/C$ catalyst oxidized hydrazine hydrate at a lower potential and exhibited higher mass activity in comparison with a similarly made Ni/C catalyst. Chemical insight suggests that the cause of improved performance for the $Ni_{0.9}La_{0.1}/C$ catalyst is likely multifunctional synergism of the components. However, X-ray absorption fine structure (XAFS) and high voltage electron microscopy (HVEM) unexpectedly show some hcp–$LaNi_5$ shells coating the fcc–Ni catalyst particles. As a result of the screening tests, an unsupported $Ni_{0.9}La_{0.1}$ catalyst was synthesized by spray pyrolysis and tested in a direct hydrazine hydrate fuel cell MEA (DHFC) producing 453 mW cm^{-2}.

1. Introduction

H_2/O_2 polymer electrolyte fuel cells (PEFCs), which use proton exchange membranes as electrolytes, have been intensively developed as a primary power source for fuel cell vehicles (FCVs) in an effort to reduce fossil fuel dependence. However, to become commercially viable PEFCs have to overcome cost and availability barriers caused by the reliance on Pt and Pt-based catalysts in both anode and cathode electrodes of FCs. The need for onboard hydrogen storage in vehicles also hinders the popularization of FCVs. Onboard hydrogen storage for a 500 km range requires the use of a high pressure tank of 70 MPa of hydrogen, presenting both a technological barrier and a major safety hazard.

In contrast with H_2/O_2 PEFCs which use proton exchange membranes, anionic polymer electrolyte fuel cells can use less expensive electrocatalysts that are based on transition metals due to the less corrosive environment inherent to alkaline systems. Also, liquid-feed fuel cell systems offer many benefits over hydrogen fuel systems because hydrogen is difficult to transport and store while the current fuel transportation infrastructure is for fluids. Different liquid fuels have therefore been studied for direct liquid automotive and portable fuel cells with different technologies relying on ethanol (DEFCs) [1], methanol (DMFCs) [2], ammonia (DAFCs) [3], borohydride (DBFCs) [4] and hydrazine hydrate (DHFCs). Recent developments in Hydrazine-Hydrate fuel cell technology have led to full-sized demonstration DHFCs indicating their feasibility and promise in future fuel cell vehicles [5–8].

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When selecting a fuel for FCVs it is of course necessary to consider safety, physical characteristic, and theoretical performance data for the specific application. Table 1 shows a summary of factors relevant for evaluating FCV fuels for the three fuels 100% hydrazine hydrate ($N_2H_4 \cdot H_2O$), anhydrous hydrazine (N_2H_4), and hydrogen (H_2). Because of widely held views on hydrazine safety, it is important to note that hydrazine hydrate has completely different properties from anhydrous hydrazine. Hydrazine hydrate is industrially used as a chemical reagent, with approximately 20,000 tons/year of hydrazine hydrate distributed in Japan regularly. Hydrazine hydrate has a freezing temperature of -50 °C which means it can be used as fuel in FCVs in cold regions and it is less volatile than alcohol fuels so that air emissions are lower. The flame point of 100% hydrazine hydrate is 74 °C at atmospheric pressure, however, at concentrations less than 60%, hydrazine hydrate is not flammable. The carcinogenic risk of hydrazine hydrate, class 2B by International Agency for Research on Cancer (IARC) report, is equivalent gasoline so careful handling of the fuel is required but not more so than currently accepted guidelines for gasoline. The relative carcinogenic safety of hydrazine is illustrated by carcinogenicity studies that found no increased cancer risk for workers in a hydrazine production plant [9,10]. As a fuel hydrazine hydrate has several benefits including safety, efficiency, and energy density as reported by W. Qian et al. [11]. Hydrazine hydrate electrooxidation leads to harmless N_2 and H_2O products, and the theoretical efficiency of DHFCs is higher than H_2/O_2 PEFCs. Further, the liquid fuel used in DHFCs has a higher energy density than H_2, and the theoretical potential of DHFCs (1.62 V) is also superior to DEFCs (1.15 V), DMFCs (1.21 V), and DAFCs (1.17 V), except for DBFCs (1.64 V), when O_2 is used for a cathode fuel [12]. Thus, hydrazine hydrate presents an attractive alternative to hydrogen for FCVs.

Electrodes for hydrazine electrooxidation reactions have been studied as early as 1960's [13–15], and much effort has been devoted to the development of new electrocatalysts for hydrazine electrooxidation for DHFCs [16–23]. We previously reported that the electrocatalytic activity of Ni and Co is higher than Pt for electrooxidation of hydrazine hydrate in alkaline environments [24]. In recent research Ni-based binary alloy catalysts such as Ni–Zn [25,26], Ni–Co [27,28], Ni–Pd [29], Ni–Ag [30], Ni–Pt [31], Ni–Zr [7], and Ni–Fe [32] were shown to improve hydrazine hydrate oxidation efficiently through alloying effects. These improved performance levels motivated us to further study Ni-alloy catalysts for use in DHFCs. Other complex catalysts were also developed for hydrazine oxidation and hydrazine derivatives oxidation including $[(bpy)_2Ru(5{-}phenNH_2)]Cl_2 \cdot H_2O$ (byp; bipyridine, phen; phenanthroline) and Co porphyrin [33,34]. Despite improvements to date, hydrazine oxidation catalysts must be further improved to meet the required catalytic activity and selectivity for the popularization of DHFCVs.

The Ni–La binary system contains various intermetallic crystal structures such as $LaNi_5$, LaNi [35] which are known to be active hydrogen absorption materials and therefore can be projected to have good hydrogen activation performance. In this study we therefore synthesized, characterized, and tested carbon supported $Ni_{1-x}La_x$ ($0.1 \le x \le 0.9$) catalysts for hydrazine hydrate oxidation in alkaline media. The results of this investigation identified $Ni_{0.9}La_{0.1}$/C as the best formulation and conjectures on the active phase are reported. The optimal formulation was then used to develop unsupported catalysts, and we present preliminary results for an unsupported $Ni_{0.9}La_{0.1}$ catalyst tested in a direct hydrazine hydrate fuel cell MEA (DHFC) producing 453 mW cm^{-2}.

2. Experimental

2.1. Catalyst synthesis

2.1.1. Impregnation/freeze-drying procedure for the catalyst screening

Ni/C, La/C, $Ni_{1-x}La_x$/C catalysts were synthesized using an impregnation/freeze-drying procedure followed by thermal annealing for the screening test. The atomic composition (as at%) of each sample was varied in 10 at% increments from (90:10) to (10:90). All catalysts samples contained 23 wt% total metal on carbon support. First, aqueous metal nitrate solutions made from precursor compounds of $Ni(NO_3)_2 \cdot 6H_2O$ (98%, Kishida Chemical) and $La(NO_3)_2 \cdot 6H_2O$ (97%, Kishida Chemical) dissolved in deionized water (>18.2 MΩ cm, Millipore Direct–Q 3 UV Water Purification System, Millipore) were impregnated with carbon black (Ketjenblack ECP600JD, Lion) by a robotic liquid dispenser (Model GX271, Gilson) utilized to pipette the desired amount of metal solution. Slurries were sonicated for 5 min and the impregnated catalysts were then immersed in liquid N_2. The cooled slurries were freeze-dried under a moderate vacuum (0.055 mbar, FreeZone, Labconco) over 40 h. All catalysts were prepared in 10 mL quartz vials. Reduction of metal precursors to the zero-valent state on the carbon support was thermally driven under a reductive H_2 atmosphere (10% H_2, balance Ar) at 250 °C for 2.5 h using a tube furnace. Final thermal annealing was performed immediately after the reduction step at 800 °C for 5 h in 10% H_2 atmosphere.

2.1.2. Spray pyrolysis for MEA anode catalyst

Synthesis of unsupported $Ni_{0.9}La_{0.1}$ catalyst was achieved using spray pyrolysis following a previously reported approach [25,26]. Metal nitrates (Ni and La) (99%, Sigma–Aldrich Co.) were dissolved

Table 1

Comparison of hydrazine hydrate ($N_2H_4 \cdot H_2O$), anhydrous hydrazine (N_2H_4), and hydrogen (H_2) properties. Including physical properties at 25 °C/1 atm, virulence, reaction equations, thermochemical data ($-\Delta H$; Enthalpy, $-\Delta G$; Gibbs free energy), theoretical potential (E^0), efficiency (ε), and energy density.

	100% hydrazine hydrate ($N_2H_4 \cdot H_2O$)	Anhydrous hydrazine (N_2H_4)	Hydrogen (H_2)
Major use	Blowing agent	Rocket fuel	Petroleum synthesis
	Deoxidizer	Aircraft fuel	Weld
	Reductant	–	Reductant
Physical condition	Liquid	Liquid	Gas
Freezing point	-51.7 °C	2 °C	-259 °C
Boiling point	121 °C	114 °C	-253 °C
Flame point	74 °C	38 °C	-157 °C
Possibly carcinogenic to humans by IARC	2B	2B	–
Toxicology (Rat)	LD50 = 129 mg kg^{-1}	LD50 = 60 mg kg^{-1}	Blackdamp
Electrochemical reaction	$N_2H_4\,(l) + O_2(g) \rightarrow N_2(g) + 2H_2O\,(l)$		$2H_2(g) + O_2(g) \rightarrow 2H_2O\,(l)$
$-\Delta H$	622 kJ mol^{-1}		286 kJ mol^{-1}
$-\Delta G$	623 kJ mol^{-1}		237 kJ mol^{-1}
E^0	1.62 V		1.23 V
ε	100%		83%
Energy density	5.4 kWh L^{-1}		0.18 kWh L^{-1} (7 MPa)