Ni Nanoparticles Supported on MIL-101 as a Potential Catalyst for Urea Oxidation in Direct Urea Fuel Cells

Ngan Thao Quynh Tran*, Hyo Sun Gil**, Gautam Das**, Bo Hyun Kim** and Hyon Hee Yoon**,†

*Department of machine and Equipment, Industrial University of Ho Chi Minh City, Nguyen Van Bao, HCMC, Vietnam
**Department of Chemical and Bio Engineering, Gachon University,
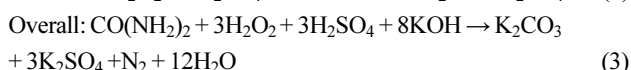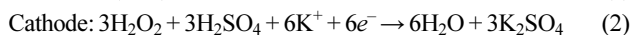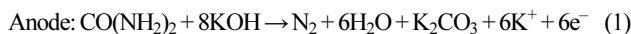*1342, Seongnam-daero, Sujeong-gu, Seongnam-si, Gyeonggi-do, 13120, Korea*

Abstract − A highly porous Ni@MIL-101catalyst for urea oxidation was synthesized by anchoring Ni into a Cr-based metal-organic framework, MIL-101, particles. The morphology, structure, and composition of as synthesized Ni@MIL-101 catalysts were characterized by X-Ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, and transmission electron microscopy. The electro-catalytic activity of the Ni@MIL-101catalysts towards urea oxidation was investigated using cyclic voltammetry. It was found that the structure of Ni@MIL-101 retained that of the parent MIL-101, featuring a high BET surface area of 916 m^2 g^{-1}, and thus excellent electro-catalytic activity for urea oxidation. A urea/H_2O_2 fuel cell with Ni@MIL-101 as anode material exhibited an excellent performance with maximum power density of 8.7 $mWcm^{-2}$ with an open circuit voltage of 0.7 V. Thus, this work shows that the highly porous three-dimensional Ni@MIL-101 catalysts can be used for urea oxidation and as an efficient anode material for urea fuel cells.

Key words: Urea oxidation, Urea fuel cell, Ni catalysts, Metal organic framework, MIL-101, Ni@MIL-101

1. Introduction

The non-toxicity, affordability, and ease of storage/transport of urea make urea fuel cells promising power sources [1,2]. In a urea/H_2O_2 fuel cell, urea is electro-oxidized at the anode (Eq. 1), while H_2O_2 is reduced at the cathode (Eq. 2):

Anode: $CO(NH_2)_2 + 8KOH \rightarrow N_2 + 6H_2O + K_2CO_3 + 6K^+ + 6e^-$ (1)

Cathode: $3H_2O_2 + 3H_2SO_4 + 6K^+ + 6e^- \rightarrow 6H_2O + 3K_2SO_4$ (2)

Overall: $CO(NH_2)_2 + 3H_2O_2 + 3H_2SO_4 + 8KOH \rightarrow K_2CO_3$
$+ 3K_2SO_4 + N_2 + 12H_2O$ (3)

The theoretical cell voltage of a direct urea/H_2O_2 fuel cell equals 2.509 V, which is higher than other types of fuel cells [3]. The H_2O_2 can be electro-reduced in basic media; however, the theoretical cell voltage is 1.63 V [4]. Moreover, oxygen can be used as cathodic oxidant with the theoretical cell voltage of 1.15 V. However, the practical implementation of the direct urea fuel cells is hindered by their relatively low power density. Hence, most research efforts are directed at the development of suitable anode catalysts to speed up the sluggish kinetics of the six-electron-transfer urea oxidation reaction [5]. Currently, non-precious Ni-based catalysts are considered as the most efficient anode materials in the urea fuel cells [5,6]. To enhance the activity and stability of the Ni-based catalysts, various metals including Co, Mo, Cr, W, and Fe have been doped [7-10] and/or composited with carbon-based nanostructures such as carbon nanotubes, graphene, and aerogels [11-14].

In this study, we propose Ni nanoparticles impregnated into highly porous three-dimensional nanostructured metal-organic frameworks (MOFs) as an efficient electro-catalyst for urea oxidation reaction in direct urea fuel cells. A Cr-based metal-organic framework, MIL 101, was chosen as the MOF because it has a high surface area and high porosity with a pore size of 2.9-3.4 nm [15-17], which makes it favorable for catalysis material because catalyst pore sizes of 2-10 nm range are known to be preferable for electrochemical applications, because not only do these pores serve as a good reaction sites, they also shorten the path length the fuel and the ions have to travel [18,19]. In addition, Cr is known to enhance the catalytic activity of Ni for urea oxidation reaction [9]. The Ni-anchored MIL-101 catalyst (Ni@MIL-101) was subjected to structural, morphological, and electrochemical characterization. The performance of a urea/H_2O_2 fuel cell comprising the Ni@MIL as anode materials was evaluated.

2. Experimental

MIL-101 was synthesized by a hydrothermal procedure [20-22]. Briefly, a mixture of $C_6H_4(CO_2H)_2$ (H_2BDC), HF, $Cr(NO_3)_3·9H_2O$, and $C_{17}H_{35}CO_2H$ in de-ionized (DI) water was placed in a 100 ml Teflon-lined autoclave at 220 °C for 8 h. After cooling to ambient temperature, the green powder was collected by centrifugation and purified by solvothermal treatment in ethanol at 80 °C for 24 h. Then, the green solid product was soaked in NH_4F solution at 70 °C for 24 h.

†To whom correspondence should be addressed.
E-mail: hhyoon@gachon.ac.kr
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After centrifuging, the final solid product (MIL-101) was dried in a vacuum oven at 70 °C overnight. The as-synthesized MIL-101 (100 mg) was mixed with 10 mL of 0.2 M $Ni(NO_3)_2 \cdot 6H_2O$ in DI water and continuously stirred overnight at room temperature. To the resulting green suspension, $NaBH_4$ and H_3NBH_3 were added under vigorous stirring at 273 K. The mixture was centrifuged and dried to yield Ni@MIL-101 particles.

To prepare catalyst inks, as synthesized catalyst powder (Ni@MIL-101) was dispersed in dimethyl formamide and mixed with a Nafion solution (Nafion 117, 5 wt% in isopropanol). After homogenization, the resulting anode catalyst ink was coated onto a carbon paper (TGP-H-60 Toray) to achieve a catalyst loading of 2 mg cm^{-2}. Similarly, a commercial Pt/C (40 wt%, E-TEK)-coated carbon paper with a Pt loading of 2 mg cm^{-2} was used as a cathode. A cation exchange membrane (Nafion 115) was used as a polymer electrolyte. A graphitic plate with serpentine flow channels and gold-coated stainless current collector were used for the single cell test. An aqueous solution of urea and KOH was fed into the anode side at a rate of 5 mL min^{-1}, and 2 M H_2O_2 in 2 M H_2SO_4 solution was supplied to the cathode a rate of 5 mL min^{-1}.

The catalyst powders were characterized using X-ray diffraction (XRD; Rigaku DMAX), Fourier transform infrared spectroscopy (FTIR; JASCO FT-IR 300E), scanning electron microscopy (SEM; Hitachi S-4700, Japan), focused ion-beam SEM (FIB-SEM; Hitachi, Japan), and transmission electron microscopy (TEM; Tecnai G2 F30 S-Twin, USA). The specific surface area and pore size distribution were measured by N_2 adsorption/desorption isotherms at liquid nitrogen temperature (77 K) on a Micromeritics ASAP 2020. The electrochemical measurements were by cyclic voltammetry (CV) using a potentiostat-galvanostat (VSP, Bio-Logic) on conventional three electrode cells setup. Ag/AgCl electrode was used as a reference electrode and a Pt wire as a counter electrode. Catalyst powder applied on carbon paper (as described above) cut into 5 mm×5 mm was used as working electrode. Fuel cell performance was evaluated utilizing the potentiostat-galvanostat interfaced with EC-lab 11.01 data acquisition software.

3. Results and Discussion

The XRD patterns of as prepared MIL-101 and Ni@MIL-101 particles are shown in Fig. 1a. The XRD patterns of MIL-101 were consistent with the simulated one with formula of $Cr_3F(H_2O)_2O$ $[(O_2C)C_6H_4(CO_2)]_3 \cdot nH_2O$ (n = ~25) (CCDC No. 605510) [23,24]. In addition, no peaks for H_2BDC were observed, confirming the successful synthesis of phase pure MIL-101(Cr). The XRD patterns of Ni@MIL-101 were intact with those of MIL-101, implying a good dispersion of Ni in the MIL-101 structure because metal nanoparticles would exhibit no characteristic peaks if dispersed as a monolayer or submonolayer [25,26]. The XRD pattern of Ni@MIL-101 was similar to those of MIL-101. Some peaks disappeared by the presence of Ni, indicating possible structural deformation of MIL-101 by the Ni.
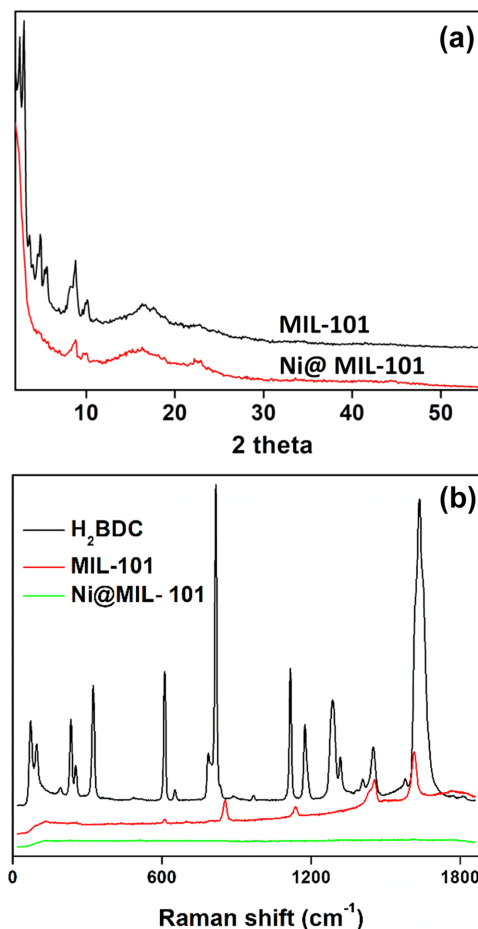
Fig. 1. XRD patterns (a) and Raman spectra (b) of MIL-101 and Ni@MIL-101.

However, no extra peak appeared by the presence of Ni, implying a good dispersion of Ni in the MIL-101 structure because metal nanoparticles would exhibit no characteristic peaks if dispersed as a monolayer or submonolayer [25,26].

A comparative Raman spectra (Fig. 1b) revealed that MIL-101 had peaks for H_2BDC but, however, Ni@MIL-101 had no peaks for H_2BDC, further indicating the successful synthesis of pure Ni@MIL-101.

Fig. 2 shows SEM, cross-sectional FIB-SEM, and TEM images of as prepared Ni@MIL-101. The cross-sectional FIB-SEM revealed that Ni@MIL-101 comprised of nano-sized subunits featured a highly porous structure. The spherical subunit particles were uniformly distributed with average sizes of ~50 nm. In addition, Ni nanoparticles, appearing as dark gray areas in TEM image, were well dispersed throughout the MIL-101 crystal, as shown in Fig. 2c. The Ni and Cr composition ratio in the Ni@MIL-101 samples was approximately 56:44 (Ni/Cr) as determined by EDX spectra (Fig. 2d).

The BET specific surface area and pore volume, determined from nitrogen adsorption-desorption isotherms as shown in Fig. 3, of the MIL-101 were 1731 m^2 g^{-1} and 0.40 cm^3 g^{-1}, respectively. After the anchoring of Ni in MIL-101, the BET specific surface area and pore volume of the Ni@MIL-101 decreased to 916 m^2 g^{-1} and 0.22 cm^3 g^{-1}, respectively, probably due to the increased density by the addition of
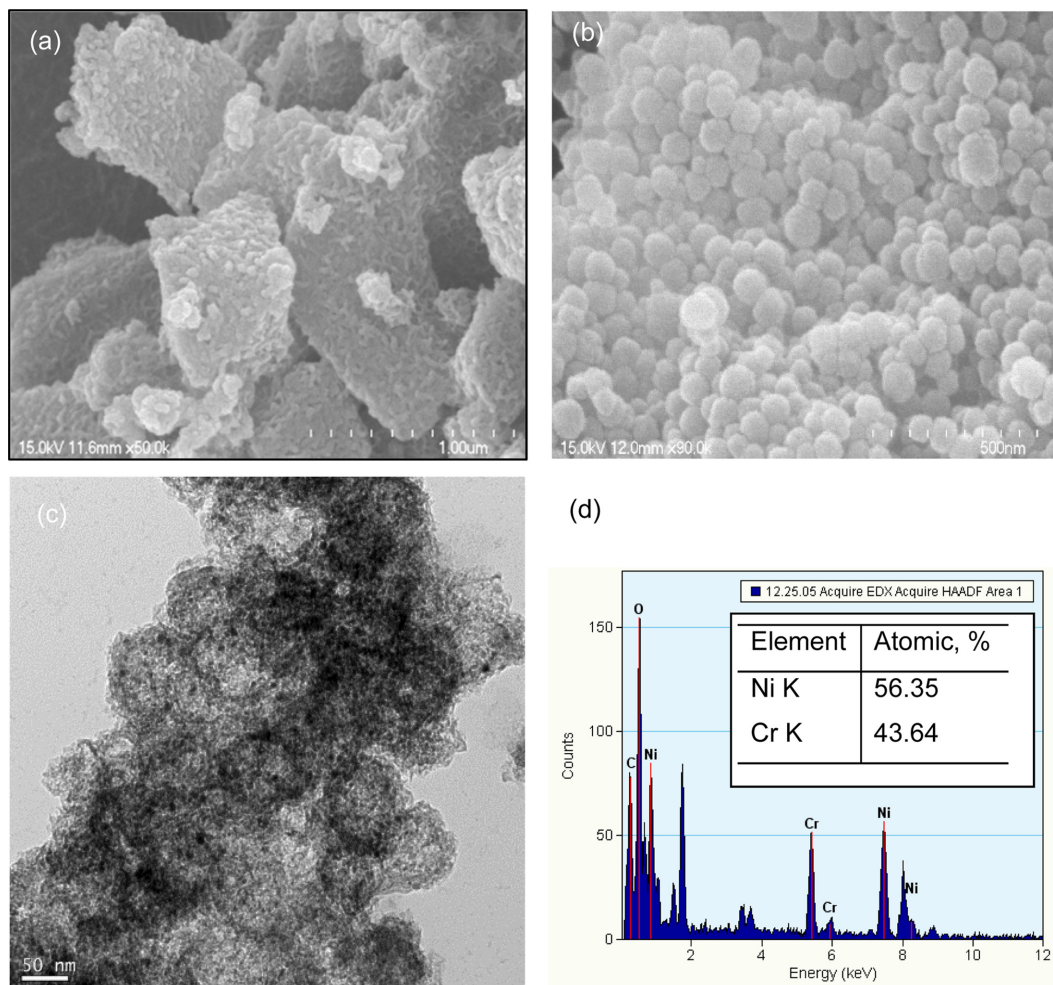
Fig. 2. SEM (a), cross-sectional FIB-SEM (b), TEM (c) images, and (d) EDX spectrum of as synthesized Ni@MIL-101 particles.
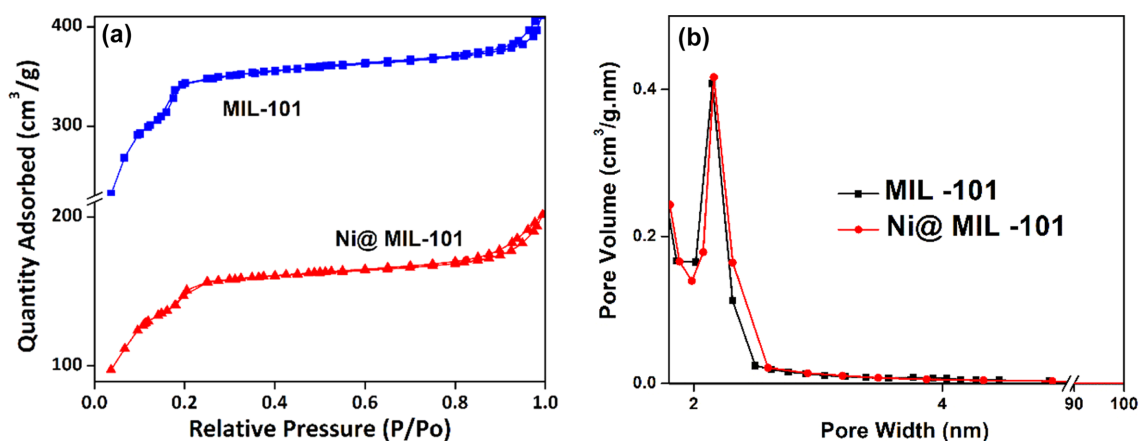
Element	Atomic, %
Ni K	56.35
Cr K	43.64

Fig. 3. N$_2$ sorption isotherm (a), and pore size distribution (b) of MIL-101 and Ni@MIL-101.

Ni and/or pore blocking by Ni particles.

The catalytic activity of Ni@MIL-101 for urea electro-oxidation was examined by cyclic voltammetry (CV) measurements as shown in Fig. 4. The CV curves of the Ni-based catalyst in the absence of urea exhibited a pair of redox peaks at 0.55~0.6 and 0.4~0.5 V vs. Ag/AgCl, which corresponded to anodic and cathodic peak potentials,

respectively, and indicated the previously reported inter-conversion of Ni^{2+}/Ni^{3+} in alkaline medium [27,28]. In the presence of 0.1 M urea in 0.1 M KOH, the Ni-based catalysts exhibited redox peaks (with increased oxidation peak intensity and decreased reduction peak intensity) at the similar potentials as those observed in 0.1 M KOH, which confirmed the activity of these catalysts for urea oxidation
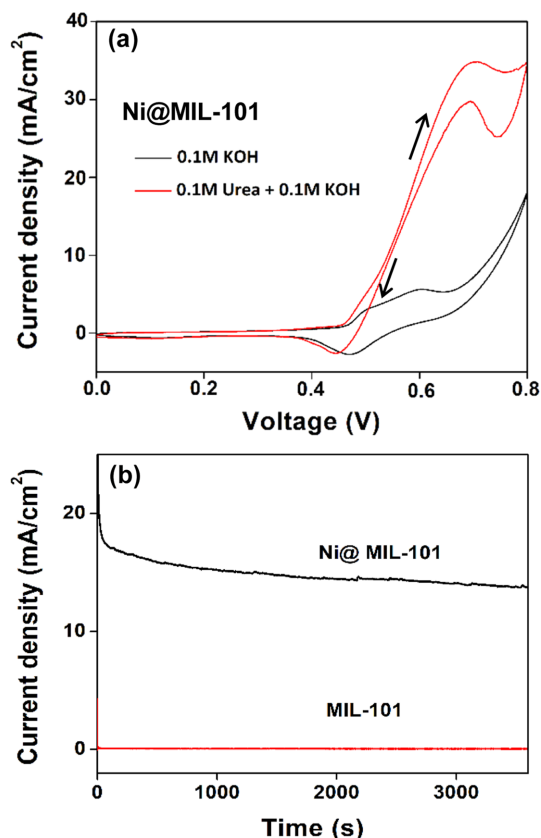
Fig. 4. (a) CV curves of Ni@MIL-101 recorded in the absence (black) and presence of 0.1 M urea (red) in 0.1 M KOH at scan rate of 10 mV s^{-1}, and (b) chronoamperometric responses of MIL-101, and Ni@MIL-101 in 0.1 M urea in 0.1 M KOH at 0.6 V.

Fig. 5. I-V and power density curves of a urea/H_2O_2 cell with Ni@ MIL-101 as anode at 0.3 M urea in 1 M KOH at 70 °C.

occurring via Ni^{2+}/Ni^{3+} redox pathway. The results, therefore, indicated that urea oxidation occurred via an indirect mechanism involving the reduction of NiOOH to $Ni(OH)_2$ and the electrochemical regeneration of $Ni(OH)_2$ to NiOOH as reported previously [12,28]. Ni@MIL-101 exhibited a higher peak current density of 35.3 mA cm^{-2}, whereas values of 14.6 mA cm^{-2} were obtained for Ni/MIL-101/bulk. The results suggested that the addition of stearic acid was critical in the preparation of suitable MIL-101 for Ni-doping. The electro-catalytic activity of Ni@MIL-101 catalyst was further examined by chronoamperometric measurements at 0.6 V in 0.1 M urea in 0.1 M KOH, as shown in Fig. 4c. The Ni@MIL-101 catalyst exhibited stable current responses.

A urea/H_2O_2 type fuel cell was fabricated using Ni@MIL-101 catalyst as anode materials. The *I-V* polarization and power density curves of this cell recorded in 0.3 M urea in 1.0 M KOH at 70 °C are shown in Fig. 5. The open circuit voltage (OCV) of the urea fuel cell was around 0.7 V, which is comparable with previously reported values (0.6-0.8V) [2,3,29]. The maximum power density was obtained as 8.7 mW cm^{-2}. The excellent performance of the Ni@MIL anode was mainly attributed to its high specific surface area and mesoporous structure, which provided a high number of active Ni-catalyst sites and allowed fast mass transfer of urea and products in the anode.
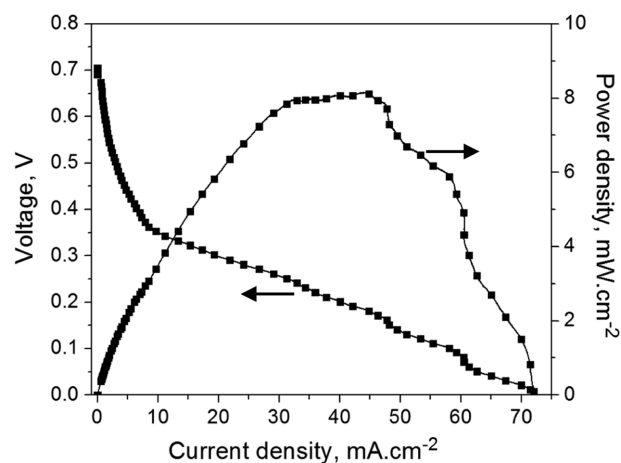
4. Conclusion

Highly porous nanostructured Ni@MIL-101catalyst for urea oxidation was synthesized by doping Ni into MIL-101 particles. The prepared Ni@MIL-101catalyst exhibited a high specific surface area and thus featured excellent electro-catalytic activity for urea oxidation. A DUFC containing Ni@MIL as an anode catalyst achieved a maximum power density of 8.7 mW cm^{-2} in 0.3 M urea and 1 M KOH at 70 °C. The result suggests that the simply prepared nanostructured Ni@MIL-101 catalysts are suitable anode materials for DUFCs.

Acknowledgment

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