Formic Acid Electro-Oxidation Catalyzed by PdNi/Graphene Aerogel

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Abstract: Direct formic acid fuel cells involve two significant half-reactions, namely formic acid electro-oxidation and oxygen reduction reaction, and the more sluggish and complex process for anode formic acid oxide also determine the whole fuel cells energy conversion efficiency. The most efficient catalysts rely on the noble metal of Pt and Pd based catalysts and compared with Pt catalysts, Pd catalyst is more appealing because of the low CO poisoning effect during the electro-oxidation of formic acid that mainly follows the direct pathway. The Pd alloy effect and support effect should be considered for the catalyst fabrication since the resulted structure and electronic modification could largely increase the catalytic performance. Graphene emerges out as novel support while the easy agglomeration and destruction of pure graphene do not guarantee promising merits. In this work, we demonstrated the formic acid oxidation ability boosting by facile coupling PdNi alloy and 3D graphene aerogel (PdNi/GA) via a freezing-drying/thermal annealing reduction approach. The PdNi alloy crystal structure was well confirmed by the X-ray diffractions technique and the alloy nanoparticles were successfully anchored on the 3D graphene aerogel surface. The electrochemical performance was evaluated for formic acid oxidation in the acid electrolyte. The PdNi/GA catalyst displayed a larger peak current density of $136 \text{ mA}\cdot\text{cm}^{-2}$, which was 2 and 3.45 times greater than Pd/GA ($68 \text{ mA}\cdot\text{cm}^{-2}$) and Pd/C ($39.4 \text{ mA}\cdot\text{cm}^{-2}$), respectively. The anti-CO poisoning ability was measured by CO stripping technique, and a low onset potential of 0.49 V was found on PdNi/GA catalyst, about 120 mV less than that of Pd/GA catalyst, indicating the oxophilic property of Ni to assist formic acid oxidation via the bi-functional mechanism. The oxidation peak potential of 0.67 V was observed on PdNi/GA, about 40 mV less than that of Pd/C catalyst, indicating the merits of 3D structure of graphene. Moreover, PdNi/GA catalyst had the highest mass activity of $1699 \text{ mA}\cdot\text{mg}^{-1}$ compared to Pd/GA ($851 \text{ mA}\cdot\text{mg}^{-1}$) and Pd/C ($537 \text{ mA}\cdot\text{mg}^{-1}$) catalysts. The specific activity of PdNi/GA was $2.6 \text{ mA}\cdot\text{cm}^{-2}$, which was 1.94 and 2.7 times of Pd/GA ($1.34 \text{ mA}\cdot\text{cm}^{-2}$) and Pd/C ($0.96 \text{ mA}\cdot\text{cm}^{-2}$) catalysts. The highly improved catalytic performance could be due to the combined alloy and support effect. The PdNi/GA was a promising catalyst for application in the direct formic acid fuel cells.

Key Words: Formic acid oxidation reaction; Direct formic acid fuel cell; Electrocatalyst; Pd-base catalyst; Graphene aerogel

PdNi/石墨烯气凝胶电催化甲酸氧化

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摘要: 甲酸电氧化性能提升对发展直接甲酸燃料电池至关重要。本文首次报道了采用简便的冷冻干燥/退火还原的方法将PdNi合金与三维石墨烯气凝胶进行了高效耦合并实现了对甲酸氧化反应的高效催化。利用X射线衍射、扫描电镜和透射

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电镜等仪器对催化剂的结构和形貌进行了表征, 并对其催化甲酸氧化反应的性能进行了研究。PdNi以合金纳米粒子形式分散在三维石墨烯气凝胶(PdNi/GA)表面, PdNi/GA催化剂中Pd的XPS能谱有明显的位移, 表明Pd, Ni和石墨烯气凝胶载体之间有较强的电子相互作用。电化学测试结果表明PdNi/GA催化剂具有很高的甲酸电氧化性能, 其峰值电流密度为 $136 \text{ mA}\cdot\text{cm}^{-2}$, 分别是Pd/GA ($68 \text{ mA}\cdot\text{cm}^{-2}$)和Pd/C ($39.4 \text{ mA}\cdot\text{cm}^{-2}$)的2倍和3.45倍。在CO溶出伏安测试中, PdNi/GA催化剂的起始电位和峰电位分别是0.49和0.67 V, 证明PdNi/GA催化剂具有优异的抗CO毒化能力。PdNi/GA良好的催化性能可以归因于石墨烯三维结构提供的优异分散性及导电性和钯镍合金抗CO中毒能力的提升。

关键词: 甲酸氧化反应; 直接甲酸电池; 电催化剂; 钯基催化剂; 石墨烯气凝胶

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1 Introduction

Formic acid electro-oxidation is a significant fundamental reaction in the development of the energy-relevant device, especially for the direct formic acid fuel cells¹⁻³. To efficiently catalyze this reaction, catalysts are required and the most efficient materials relied on the noble metal of Pt and Pd based catalysts^{4,5}. It was recognized that Pt catalysts exhibited poor catalytic performance arising from CO poisoning accumulated by the dehydration step⁶⁻⁸. Compared with Pt catalysts, the electro-oxidation of formic acid on Pd catalysts is mainly performed through the direct pathway, thus it has a very low CO poisoning effect⁹. Therefore, lots of researches have been done on Pd by structure/morphology/composition modifying with other materials, yet challenging is still faced for the anti-CO poisoning ability promotion.

Alloying with transition metals is regarded as an effective way to enhance the catalytic capability for formic acid electro-oxidation. Attention has been directed to the surface modification, shape engineering, and structure optimization for this kind of catalysts^{10,11}. The resulted alloyed catalyst exhibited superior catalytic performance to that of its single counterpart, because of the electronic modification resulting from the lowered D-band center¹². Moreover, the oxophilic property of the second element could readily promote the formation of oxygen-containing species at a low potential as interpreted by the bifunctional mechanism for the poisoning intermediates oxidation-removal^{13,14}. That could be interpreted simply in the below mechanism for a Pd-M (metal) alloy catalyst.

Furthermore, the catalytic structure and the support material also have a great impact on the catalytic activity. To further increase the utilization of the catalytic active sites, one efficient strategy is to disperse Pd based nanoparticles onto suitable support with large surface area and good electrical conductivity¹⁵. The traditional carbon-based support has been intensively employed such as the carbon black, carbon nanotube, carbon fiber; and the Vulcan XC 72R carbon is currently commercially applied^{16,17}. Graphene is an ideal support for advanced catalysts because of its peculiar 2D nature and single-atom thickness, high chemical stability and ultra-high thermal conductivity^{18,19}.

Some reports have been released on graphene support Pd catalyst for formic acid oxidation, while no amazing catalytic performance was realized probably due to the easy agglomeration and destruction of pure graphene^{15,20}.

Luckily, graphene aerogel (GA), a rising star material, could overcome the above-mentioned problems by self-assembled 2D individual graphene sheets into 3D graphene aerogels^{21,22}. Besides the virtues of the graphene alone, 3D graphene aerogel also exhibits several inherent merits including the efficient ions and molecules transportation and diffusion, large surface area, high electrical conductivity and chemical or electrochemical stability^{23,24}. Therefore, they have potential applications in varied fields like energy storage, sensors, catalyst supports, etc^{25,26}. Based on our experience, the ample oxygen-containing functional groups and conjugated domains might be useful for the formic acid molecular oxidation. To the best of our knowledge, rare reports are available in this field.

Platinum or Pd nanoparticles supported on heteroatom doped 3D graphene aerogel was tried for formic acid and methanol oxidation^{27,28}, while the performance was still not satisfactory because of insufficient oxophilic species formation. By coupling the above inspirations, herein, we tried to fabricate the hybrid PdNi/graphene aerogel (PdNi/GA) catalyst by a simple freezing-drying/annealing approach to probe the formic acid oxidation ability. Because of the above mentioned many advantages, the as-fabricated PdNi/GA catalyst displayed a very high catalytic efficacy to formic acid electro-oxidation. The high catalytic ability could be due to the larger surface provided by the 3D structure of graphene and the oxygen-containing groups on the graphene aerogel, which were beneficial to the removal of CO_{ad} generated during the formic acid oxidation. This work provides a promising hybrid catalyst for direct formic acid fuel cells and extends the application of graphene aerogels.

2 Experimental

2.1 Reagent

All chemicals were purchased and used without further purification. Nickel acetate tetrahydrate ($\text{NiC}_4\text{H}_6\text{O}_4\cdot 5\text{H}_2\text{O}$, AR), Palladium chloride acid (H_2PdCl_4 , $30 \text{ mg}\cdot\text{mL}^{-1}$), Nafion (AR), were purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD. Graphene was provided by the Institute of Coal Chemistry, Chinese Academy of Sciences. Milli-Q water

(Thermo Fisher Scientific (USA) Co., Ltd) was used throughout the experiments.

2.2 Catalyst fabrication

PdNi/GA was synthesized in the following steps: 30 mg graphene was added into 6 mL H₂O with ultrasonic treatment for 1 h. Then 40 mg Nickel acetate tetrahydrate and 317 μ L Palladium chloride acid were added into the solution with a constant stir. The final solution was freeze-dried for 48 h. The resulting black solid sample was annealed in H₂ atmosphere at 500 °C for 2 h with a heating rate of 5 °C·min⁻¹²⁹. The reference sample of Pd/GA was prepared with the same procedure without the addition of Nickel acetate tetrahydrate. A home-made Pd/C catalyst was also compared⁹. The Pd loading for all the catalyst was 20% (mass fraction).

2.3 Characterization

The sample was characterized on Bruker D8 advance X-ray diffraction (XRD) with Cu K α radiation. The morphology was examined with a FEI Sirion-200 scanning electron microscope (SEM) and a transmission electron microscope (TEM) operating at 200 kV. X-ray detector spectrum (EDS) images were obtained on a TECNAI G2 F30 transmission electron microscope (acceleration voltage: 300 kV). X-ray photoelectron spectroscopy (XPS) measurement was carried on an ECSALAB250Xi spectrometer with an Al K α radiation source.

2.4 Electrochemical measurements

All the electrochemical measurements were carried out in a conventional three electrode electrochemical cell by using an electrochemical workstation INTERFACE 1000 potentiostat/galvanostat (GAMRY INSTRUMENTS Co. USA). The saturated calomel electrode (SCE, Hg/Hg₂Cl₂) was used as the reference electrode. All of the potentials are relative to the SCE electrode. The graphite rod and the catalyst coated glassy carbon electrode (diameter $d = 3$ mm) served as counter and working electrode, respectively. The catalyst ink was prepared as follows. 5 mg catalyst and 50 μ L of 5% (mass fraction) Nafion solution was dispersed in 950 μ L of ethanol by sonication for at least 30 min to form a homogeneous ink. Then 10 μ L of the catalyst ink was loaded onto a pre-cleaned working electrode and let it dry naturally. The Pd loading on the glassy carbon electrode was 0.08 mg·cm⁻².

Cyclic voltammetry was carried out at room temperature in 0.5 mol·L⁻¹ H₂SO₄ containing a 0.5 mol·L⁻¹ HCOOH solution at the potential range between -0.2 and 1 V (vs SCE). The mass activity was calculated by normalizing the raw current to the Pd mass in the catalysts on the working electrode. Chronoamperometry (CA) experiment was performed in 40 mL of 0.5 mol·L⁻¹ H₂SO₄ containing 0.5 mol·L⁻¹ HCOOH solution at 0.1 V for 3600 s. The electrochemical impedance spectrum (EIS) was done at 0.1 V to probe the charge transfer resistance recorded at the frequency range from 1000 kHz to 10 mHz with 15 points per decade. The amplitude of the sinusoidal potential signal was 5 mV. CO_{ad} stripping voltammetry was measured in a 0.5 mol·L⁻¹ H₂SO₄ solution. CO was purged into the H₂SO₄ solution when the working electrode was kept at 0 V (vs SCE) for 15 min to allow the complete adsorption of CO onto the catalyst, and excess CO in the electrolyte was purged out with N₂ for 15 min. The amount of CO_{ad} was evaluated by the integration of the CO_{ad} stripping peak, assuming 420 μ C·cm⁻² of coulombic charge required for the oxidation of adsorbed CO monolayer^{30,31}. The electrochemically active surface area (ECSA) could be calculated with the following equation:

$$ECSA = Q/SI$$

where Q is the coulombic charge (in mC) obtained from the CO-stripping curve. I is the loading of Pd on the surface of the electrode (in mg) and S is a proportionality constant of 420 μ C·cm⁻².

3 Results and discussion

The hybrid PdNi/GA catalyst fabrication approach was shown in Fig. 1a, that includes the graphene aerogel (GA) formation containing the Pd and Ni precursors and the subsequent thermal reduction of Pd²⁺ and Ni²⁺ at 500 °C in the H₂ atmosphere (details see ESI). The crystalline structure of the concerned catalysts was probed by the powder X-ray diffraction (XRD) Technique (Fig. 1b). A home-made Pd/C and Pd/GA catalysts were used as control samples for comparison, and they both exhibited the face-centered cubic (fcc) structure of Pd with the characteristics peaks at 40.1°, 46.6° and 68.1° from the (111), (200) and (220) crystalline planes³². The (002) facet of carbon support was indicated by the broad peak at 25° for Pd/C and the

Fig.1 (a) The schematic diagram of synthetic procedure of PdNi/GA catalyst. (b) XRD pattern of PdNi/GA, Pd/GA and Pd/C catalysts.

sharp peak at 21° of Pd/GA catalyst was due to the increased graphite degree of graphene after annealing. This peak was also indicated on PdNi/GA catalyst and three main peaks were visible representing the PdNi alloy formation (PDF: 65-9444). The main diffraction peaks shifted to higher 2θ values relative to Pd/GA catalysts, indicating the occurrence of a lattice contraction by forming PdNi alloy³³.

The morphology of PdNi/GA catalyst was further characterized by the scanning electron microscope. An interconnected 3D graphene network was displayed and PdNi alloy particles were visible by zooming in on the image (Fig. 2a, b). The interconnected 3D structure of PdNi/GA was further confirmed by transmission electron microscopy (TEM) images (Fig. S1, Supporting Information (SI)). Nano particles were found in TEM image and the average particle size of 7.7 nm was indicated by the particle size distribution histogram (Fig. 2c and inset). The high-resolution TEM (HRTEM) image showed the interplanar spacing of 0.215 nm from the (111) facet of PdNi alloy, and the lattice fringe of 0.34 nm was indicated by the graphene layer (Fig. 2d). The selected area electron diffraction (SAED) showed the polycrystalline character with the evident spots and rings which can be indexed to the planes of PdNi (111), Pd (220), Pd (200), Pd (311) and Pd (420) in Fig. 2e. The X-ray detector spectrum (EDS) showed the concerned elements of Pd, Ni, C and O, and Cu was obviously from the copper support employed for the morphology observation (Fig. 2f). The distribution of these elements in the hybrid catalyst was demonstrated by the randomly selected areas of element mapping analysis (Fig. 2g–k).

The surface chemical state of PdNi/GA was analyzed by X-

ray photoelectron spectroscopy (XPS). The binding energy for all the spectrum was calibrated by the main peak of C 1s at 284.6 eV³⁴ (Fig. S2a (SI)) and the atomic percentage of Pd and Ni content on the surface was found to be 1 : 1 (Table S1 (SI)). The percentage of C—O of PdNi/GA was the highest, the existence of —OH was helpful for the removal of CO_{ad} as well as the performance boosting for formic acid oxidation (Table S2 (SI)). The high resolution Pd 3d spectrum included two bands of Pd 3d_{5/2} and 3d_{3/2}, and each band can be deconvoluted into Pd (0) and Pd (II) species³⁵. The binding energy shifted to a higher value was also found by comparing Pd/GA and Pd/C catalysts, indicating the much stronger support interaction of the GA than the carbon; because of the alloying effect, the binding energy of PdNi/GA also shifted to the higher binding energy direction compared with Pd/GA catalyst (Fig. 3a). This observation was consistent with previous reports about the PdNi alloy³⁶, and the shift has been attributed to more *d*-band vacancies of Ni than Pd, which would withdraw electrons from Pd and consequently increase the binding energy of Pd. For all the Pd spectra, the metallic Pd played a dominant role on the surface composition that might serve as the active sites for formic acid molecular adsorption and dissociation (Table S3 (SI)). Two components of Ni 2p_{3/2} and Ni 2p_{1/2} were visible for the spin-orbit splitting of high resolution Ni 2p spectra (Fig. 3b). Each component was fitted by metallic Ni (0), Ni (II) and the satellite peaks. The metallic Ni from the PdNi alloy sat at 852.5 and 869.8 eV respectively for 2p_{3/2} and 2p_{1/2}, and the Ni (II) from the surface oxidation was visible at 855.3 and 873.2 eV correspondingly. The easy formation of the Ni oxide species was thought beneficial to the oxygen-containing species generation during

Fig. 2 (a, b) SEM images of PdNi/GA with different resolution. (c) TEM image of PdNi/GA (inset: particle size distribution histogram). (d) High-resolution TEM, (e) SAED and (f) EDS of PdNi/GA. (g) STEM and elemental mapping images of the PdNi/GA catalyst, (h) C, (i) N, (j) Ni, (k) Pd, (l) O.

Fig. 3 (a) XPS spectra of Pd 3d for PdNi/GA, Pd/GA and Pd/C catalysts, (b) XPS spectra of Ni 2p for the PdNi/GA catalyst.

Fig. 4 (a) Cyclic voltammery curves of PdNi/GA, Pd/GA and Pd/C catalysts in 0.5 mol·L⁻¹ H₂SO₄/0.5 mol·L⁻¹ HCOOH solution at a scan rate of 50 mV·s⁻¹; (b) the corresponding Tafel plots for PdNi/GA, Pd/GA and Pd/C catalysts; (c) Nyquist plots and (d) chronoamperometry curves of PdNi/GA, Pd/GA and Pd/C catalysts in 0.5 mol·L⁻¹ H₂SO₄/0.5 mol·L⁻¹ HCOOH solution (inset of Fig. 4c: equivalent circuit).

the oxidation process as confirmed by the following CO stripping experiment and these species played an important role for the poisoning intermediates oxidation removal according to the bi-functional catalytic mechanism.

The electrochemical behaviors of these catalysts were compared in the background solution, and polycrystalline Pd behaviors were observed including the hydrogen ad/desorption peaks and Pd oxide and reduction peaks and a flat double layer range (Fig. S3 (SI)). The formic acid oxidation ability was probed by the cyclic voltammograms of PdNi/GA, Pd/GA and Pd/C in 0.5 mol·L⁻¹ H₂SO₄/0.5 mol·L⁻¹ HCOOH solution (Fig. 4a). The catalytic merits can be evaluated by the peak current density, among the studied catalysts, PdNi/GA catalyst displayed the highest peak current density of 136 mA·cm⁻², which was 2 and 3.45 times of that of Pd/GA (68 mA·cm⁻²) and Pd/C (39.4

mA·cm⁻²), respectively. Additionally, the current density of PdNi/GA was also superior or comparable to those of most recently reported Pd based catalysts (Table S4 (SI)). Tafel slope was achieved by fitting the Tafel range of the quasi-static linear scanning voltammery curve at a low scanning rate of 5 mV·s⁻¹. The Tafel slope of PdNi/GA catalyst was 64 mV·dec⁻¹, smaller than that of Pd/GA (93 mV·dec⁻¹) and Pd/C (158 mV·dec⁻¹) catalyst (Fig. 4b). The Tafel slope with the value of 60 mV·dec⁻¹ indicated the catalytic mechanism determined by dehydrogenation process³⁷ and subsequent oxidation of adsorbed CO^{38,39}. The kinetics can also be analyzed by the slope from the linear fitting of the peak current vs. the square root of the scan rates (Fig. S4 (SI)), and the larger value of 9.7 was obtained on PdNi/GA catalyst, indicating much higher catalytic kinetics. The charge transfer resistance was analyzed by

electrochemical impedance spectroscopy (EIS) recorded for formic acid oxidation at 0.1 V (Fig. 4c). Generally, the charge transfer resistance could be indicated by the semicircle in the intermediate frequency region, the larger the diameter, the larger the charge transfer resistance. The details could be obtained by EIS data fitting to display the information of the electrode-catalyst-electrolyte interface. An equivalent circuit (inset of Fig. 4c) was used that included the general electrical elements. The element of L was from the inductance of an external circuit, and R_s symbolized the uncompensated solution resistance, R_{CT} was for the charge transfer resistance and R_0 came from the contact resistance between the catalyst and the glassy carbon electrode, and constant phase elements (CPE) of double layer capacitor were required for the fitting. The uncompensated solution resistance (R_s) was about $6.8\ \Omega$ for all the electrode indicating a fair comparison, and the smallest R_{CT} value of $206\ \Omega$ for PdNi/GA catalyst indicated the fastest charge transfer ability (Table S5 (SI)). The stability of the catalysts was evaluated by the chronoamperometry (CA) experiment for 3600 s at the constant potential of 0.1 V (Fig. 4d). After the 3600 s test, the final current density is $5\ \text{mA}\cdot\text{cm}^{-2}$ for PdNi/GA, which was 1.87 and 2.8 times of Pd/GA ($2.67\ \text{mA}\cdot\text{cm}^{-2}$) and Pd/C ($1.8\ \text{mA}\cdot\text{cm}^{-2}$) catalysts, respectively. Though PdNi/GA catalyst showed much better stability than Pd/GA and Pd/C catalysts, further effort is still in need.

The anti-poisoning ability of the high-performance catalyst for formic acid oxidation was very important. Here, the anti-CO poisoning ability was examined by CO-stripping technique and the amount of catalytic active sites was estimate by electrochemical active surface area (ECSA). The onset and peak oxidation potential of adsorbed CO (CO_{ad}) could be used to evaluate the anti-poisoning ability; the lower potential represents the higher CO_{ad} oxidation ability and the higher anti-poisoning ability. Fig. 5 showed the CO stripping curves on PdNi/GA, Pd/GA and Pd/C catalysts. In the lower potential region ($-0.2 - 0\ \text{V}$) of the first sweep cycle, the absence of hydrogen desorption peaks confirmed the CO adsorption on the active sites. By increasing the potential with the positive sweep, the CO oxidation peaks were observed on all the electrodes. However,

Fig. 5 CO_{ad} stripping voltammograms of PdNi/GA, Pd/GA and Pd/C in $0.5\ \text{mol}\cdot\text{L}^{-1}\ \text{H}_2\text{SO}_4$ solution at the scan rate of $20\ \text{mV}\cdot\text{s}^{-1}$.

the CO oxidation peaks disappeared and the hydrogen adsorption/desorption peaks recovered in the second sweep cycle, indicating the adsorbed CO on the surface of catalysts was completely oxidized. The ECSAs of PdNi/GA, Pd/GA, and Pd/C catalysts were calculated to be 65.12, 63.50, and $56.00\ \text{m}^2\cdot\text{g}^{-1}$. Namely, PdNi/GA possessed much larger ECSA than Pd/GA and Pd/C catalysts, thereby offering more active sites for FAOR⁴⁰. The GA supported Pd and PdNi catalyst possessed similar ECSA but larger than that of carbon supported Pd catalyst, which might result from the 3D structure of graphene aerogel, which could provide a larger surface to support and expose the active sites. PdNi/GA showed the lowest onset potential of 0.49 V and oxidation peak potential of 0.67 V for CO oxidation (Table S6 (SI)), which indicated the highest anti-poisoning ability. The mass activity and specific activity were also calculated for the catalytic efficiency evaluation. PdNi/GA catalyst had the highest mass activity of $1699\ \text{mA}\cdot\text{mg}^{-1}$ compared to Pd/GA ($851\ \text{mA}\cdot\text{mg}^{-1}$) and Pd/C ($537\ \text{mA}\cdot\text{mg}^{-1}$) catalysts. The specific activity of PdNi/GA was $2.6\ \text{mA}\cdot\text{cm}^{-2}$, which was 1.94 and 2.7 times of Pd/GA ($1.34\ \text{mA}\cdot\text{cm}^{-2}$) and Pd/C ($0.96\ \text{mA}\cdot\text{cm}^{-2}$) catalysts (Fig. S5 (SI)).

4 Conclusions

Herein, PdNi/GA catalyst fabricated by a simple freezing-drying/annealing approach was demonstrated to have high catalytic efficiency for formic acid electrooxidation. The 3D structure of graphene aerogel could provide a larger surface to support and expose active PdNi alloy and the oxophilic property of graphene aerogel and Ni species are beneficial to the poisoning intermediates removal during the formic acid oxidation. Driven by the binary synergism and electronic effect, PdNi/GA catalyst displayed a larger peak current density of $136\ \text{mA}\cdot\text{cm}^{-2}$, which was 2 and 3.45 times greater than Pd/GA ($68\ \text{mA}\cdot\text{cm}^{-2}$) and Pd/C ($39.4\ \text{mA}\cdot\text{cm}^{-2}$), respectively. The high activity and stability make it have potential applications in direct formic acid fuel cell if properly optimized.

Supporting Information: available free of charge via the internet at <http://www.whxb.pku.edu.cn>.

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