

## Metal-Catalyst-Free Carbohydrazide Fuel Cells with Three-Dimensional Graphene Anodes

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As a potential solution to concerns on sustainable energy, the wide spread commercialization of fuel cell has long been hindered by limited reserves and relatively high costs of metal catalysts. 3D graphene, a carbon-only catalyst prepared by reduction of carbon monoxide with lithium oxide, is found to electrochemically catalyze carbohydrazide oxidation reaction efficiently. A prototype of a completely metal-catalyst-free anion exchange membrane fuel cell (AEMFC) with a 3D graphene anode catalyst and an N-doped CNT (N-CNT) cathode catalyst generate a peak power density of 24.9 mW cm<sup>-2</sup>. The average number of electrons electrochemically extracted from one carbohydrazide molecule is 4.9, indicating the existence of C–N bond activation, which is a key factor contributing to high fuel utilization efficiency.

Catalysts using precious metals, such as platinum, palladium, gold, and rhodium, are one of the most expensive components of low-temperature fuel cell. To explore sustainable energy solutions, there is an urgent need to design highly efficient and cost-effective catalytic materials for the conversion of the chemical energy stored in chemicals into electricity. So far, on the cathode side of low-temperature fuel cells, catalysts for the oxygen reduction reaction (ORR) have evolved from noble metal (platinum) to non-noble metal (Me) Me/N/C macrocycle composites,<sup>[1-3]</sup> and finally to metal-free nitrogen-doped carbons.<sup>[4,5]</sup> On the anode side, research interest was first focused on a reduction of the noble-metal loading, and later on replacement with non-noble-metal catalysts for electro-oxidation of hydrogen,<sup>[6,7]</sup> alcohol,<sup>[8,9]</sup> and hydrazine.<sup>[10,11]</sup> Nevertheless, it is still very challenging to replace metal catalysts on the anode

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side of low-temperature fuel cells by non-metal catalysts, followed by achieving the total removal of metal catalysts from fuel cells.

Although serving as metal-free heterogeneous catalyst (in carbocatalysis),<sup>[12,13]</sup> carbon, which is inexpensive, abundant, and (electro)chemically stable, has been widely used as inert catalyst support in fuel cell anodes. Since its discovery,<sup>[14]</sup> graphene has been regarded as a rising star in various areas of science and engineering.<sup>[15]</sup> Aimed at developing completely metal-catalyst-free fuel cells, three-dimensional graphene (3D graphene) carbon materials have been proposed as fuel cell anode catalysts for oxidation reactions. Because carbon is free from poisoning by many chemicals, such as CO-like reaction intermediates and sulfur, future fuel cells with graphene anode catalysts could utilize unpurified crude chemicals as fuel. Moreover, the use of metal nanoparticles as fuel cell catalysts entails agglomeration issues, which would also be solved by adopting graphene carbon material.

So as to employ metal-free graphene materials as fuel cell anode catalyst, an active fuel with a strong reducing capability is required to ensure an oxidation reaction with sufficiently high thermodynamic electromotive force. As a high-energy molecule, hydrazine contains readily activated N-H bonds, rendering it a suitable potential fuel for anion exchange membrane fuel cells (AEMFCs) without noble-metal catalyst. Specifically, nickel-based anode catalysts dominate the state-of-theart of low-temperature direct hydrazine/oxygen fuel cells (Supporting Information, Table S1). Despite high reactivity, hydrazine's high toxicity to the central nerve system of human remains a real concern for its extensive applications. With a volumetric energy density of 4.2 kWh L<sup>-1</sup>, carbohydrazide is a nontoxic alternative to hydrazine because the equilibrium electromotive force under standard conditions of carbohydrazide/O<sub>2</sub> fuel cell (+1.65 V) calculated from thermodynamic data<sup>[16]</sup> is superior to those of hydrazine/O<sub>2</sub> ( $\pm$  1.62 V), ethanol/O<sub>2</sub> (i.e., < +1.17 V), and H<sub>2</sub>/O<sub>2</sub> fuel cells (+1.23 V); see (Table 1).

${\rm CH_6N_4O} + 8{\rm OH^-} \rightarrow {\rm CO_2} + 7{\rm H_2O} + 2{\rm N_2} + 8{\rm e^-}$	(1)	
$E^\circ = -1.25 \text{ V} \text{ vs SHE}$	(1)	
$2O_2 + 4H_2O + 8e^- \to 8OH^-$	(2)	
$E^\circ = +0.40 \text{ V} \text{ vs SHE}$	(Z)	

$$CH_6N_4O + 2O_2 \to CO_2 + 3H_2O + 2N_2$$
(3)

 $E^{\circ} = +1.65 \text{ V}$ 

Table 1. Thermodynamic data of different oxygen-based fuel cells.										
Fuel	Final product	<i>n</i> <sup>[a]</sup>	<i>E</i> <sub>0</sub> <sup>[b]</sup> [V]	$W_{e}^{[C]}$ [kWh L <sup>-1</sup> ]	$\eta_{ m e}^{ m [d]}$ [%]	$\eta^{[e]}$ [%]				
hydrogen	H₂O	2	1.23	2.6 (liquid)	100	83.3				
ethanol	acetic acid	4	1.17	2.1	33.3	91.8				
	CO <sub>2</sub>	12	1.14	6.4	100	96.9				
hydrazine	N <sub>2</sub>	4	1.62	3.5 (hydrate)	100	99.9				
carbohydrazide	$\rm CO_2\!+\!N_2$	8	1.65	4.2 (solid)	100	95.6				
[a] Number of electrons extracted from a single reactant molecule.										

[b] Equilibrium electromotive force under standard condition. [c] Volumetric density. [d] Electron efficiency. [e] Thermodynamic efficiency  $\Delta G/\Delta H$ .

Full oxidation of carbohydrazide generates 8 electrons per carbohydrazide molecule [Eqs. (1)-(3)] with a thermodynamic efficiency of 95.6% (Table 1).

In the present work, taking into account materials and reaction factors, metal-catalyst-free fuel cells are designed for exploiting three-dimensional graphene (3D graphene) anode catalyst with crater-shaped projection for the electrocatalytic carbohydrazide oxidation reaction (CBOR). Among all tested samples, the 3D graphene exhibits the highest peak current density in a half cell as well as the highest peak power density (PPD) in a single cell. A prototype of a completely metal-catalyst-free AEMFC with a 3D graphene anode catalyst and a nitrogen-doped carbon nanotube (N-CNT) cathode catalyst is demonstrated.

As shown in Figure 1a, the crater-structured nanoscale cells on 3D graphene protrude from the basal plane, thereby increasing the surface area of each single graphene sheet. The 3D graphene (Figure 1a) greatly differs from graphene nanoplatelets with a flat micrometer-scale 2D structure (Supporting



**Figure 1.** Bright field transmission electron microscopy (TEM) images of 3D graphene treated with a) diluted hydrochloride acid, and b) concentrated hydrochloride acid. Dark field TEM images of c) 3D graphene and d) enlarged local area.

Information, Figure S1). Moreover, by comparing Figure 1 a and Figure 1 b, it can be concluded that diluted hydrochloric acid maintains the dedicated crater-shaped projections on 3D graphene and avoids agglomeration while concentrated hydrochloric acid does the opposite. The diameters of these crater-shaped projections were further investigated by dark-field transmission electron microscopy (TEM) (Figure 1 c and Figure 1 d), and measured to be between 60 nm to 150 nm while their thickness ranged from 7 nm to 20 nm.

Cyclic voltammetry results show that carbon is active towards CBOR (Figure 2). The activity sequence, in terms of peak



Figure 2. Cyclic voltammograms of 3D graphene, 2D graphene, and glassy carbon for carbohydrazide oxidation in  $N_2$ -purged  $1.0\,$  M KOH $+\,0.1\,$ M carbohydrazide at 50 mV s^{-1} at RT.

current density and onset potential, is 3D graphene (20.1 mA cm<sup>-2</sup> and -0.42 V) > 2D graphene (10.2 mA cm<sup>-2</sup> and -0.32 V) > glassy carbon (6.1 mA cm<sup>-2</sup> and -0.21 V). These differences are due to the different catalyst layer structures of 3D graphene (3D microscale catalyst layer with nanoscale cells), 2D graphene nanoplatelets (microscale flat surface), and glassy carbon electrode (bulk flat surface).

The electrocatalytic properties of carbon towards CBOR were then evaluated in AEMFCs with a metal-free carbon (carbon cloth, 2D graphene or 3D graphene) anode catalyst and a noble-metal-free iron-based cathode catalyst (Acta 4020) (Figure 3a). The open circuit voltage (OCV) of the direct carbohydrazide AEMFC with the 3D graphene anode catalyst was 0.594 V, which is 21 mV higher than that with 2D graphene (0.573 V) and 41 mV higher than that with a carbon cloth blank substrate (0.553 V). The PPD of the direct carbohydrazide AEMFC with the 3D graphene anode catalyst was 75.2 mW cm<sup>-2</sup>, which is 78% higher than that with 2D graphene and 5.9 times that obtained with a blank carbon cloth substrate. The consistent results shown in both half-cell and single-cell tests reveal the mass activity sequence toward CBOR for direct carbohydrazide AEMFCs is 3D graphene > 2D graphene > bulk carbon substrate (glassy carbon or carbon cloth), which can mainly be attributed to two factors: catalytic activity (associated with surface area and electrode structure)

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**Figure 3.** a) Polarization and power density curves of direct carbohydrazide AEMFCs with different carbon anode catalysts. Anode fuel: 6.0 M KOH, 1.0 M carbohydrazide,  $4.0 \text{ mLmin}^{-1}$ ; temperature (anode fuel/cathode fuel/cell): 25/80/80 °C. b) Ohmic resistance of fuel cell corresponding to Figure 3 a. c) Polarization and power density curves of AEMFC with 3D graphene anode catalyst operated under different concentration of KOH. d) Chronoamperometry curve for analysis of the average number of electrons electrochemically extracted per carbohydrazide molecule during carbohydrazide oxidation reaction (CBOR) catalyzed by 3D graphene anode catalyst in AEMFC. Anode fuel: 6.0 M KOH + 1.0 M carbohydrazide,  $4.0 \text{ mLmin}^{-1}$ ; Cell voltage: 0.25 V; cell temperature:  $60 ^{\circ}$ C. Other testing conditions for all the experiments above: Anode catalyst loading:  $5 \text{ mg}_{catalyst} \text{ cm}^{-2}$ ; Cathode catalyst: Fe-based catalyst (Acta 4020, 3 mg cm<sup>-2</sup>); AEM: Tokuyama A901; cathode fuel:  $200 \text{ mLmin}^{-1} \text{ O}_2$ , ambient pressure.

and electronic conductivity. The specific surface area of 3D graphene (151 m<sup>2</sup>g<sup>-1</sup>) is larger than that of 2D graphene (125 m<sup>2</sup>g<sup>-1</sup>). Additionally, the projections on 3D graphene function as spacers to form a 3D electrode structure, leading to an even greater number of catalytically active sites for CBOR. The Ohmic resistance (IR; Figure 3 b) of the AEMFC with the 3D graphene as anode catalyst (10 m $\Omega$ ) was lower than that with 2D graphene (16 m $\Omega$ ) and carbon cloth substrate (70 m $\Omega$ ), indicating higher electrical conductivity of 3D graphene, which gave rise to the higher performance of the AEMFC with the 3D-graphene anode, especially when compared to the performance for the carbon fiber cloth-substrate based anode.

The performance of the direct carbohydrazide AEMFC with the 3D graphene anode catalyst was also dependent on KOH concentration (Figure 3 c). Cell voltage increased with increasing KOH concentration over all current regions up to 6.0 MKOH, but further increasing the KOH concentration to 9.0 M resulted in a drop of fuel-cell performance. This trend is attributed to the balance between facilitated deprotonation of carbohydrazide by higher KOH concentration and the reverse-parabolic relationship between KOH concentration and the IR of the fuel cell. When the KOH concentration was increased from 0 M to 12.0 M at  $60 \,^{\circ}$ C, the corresponding electrical conductivity of the KOH water solution reached a maximum at 6.0-7.0 M,<sup>[17]</sup> resulting in a reverse-parabolic trend of IR with KOH concentration (Supporting Information, Figure S2).

Fuel utilization efficiency for the CBOR was evaluated after verifying the feasibility of the AEMFC with the metal-catalystfree 3D graphene anode. Unlike hydrazine, the carbohydrazide molecule has two C-N bonds and one C=O bond, in addition to N-H and N-N bonds. Cleavage of C-N bonds is essential for complete oxidation of carbohydrazide and achieving optimal fuel utilization efficiency. The fuel utilization efficiency is reflected by the average number of electrons transferred per carbohydrazide molecule, which is determined by carbohydrazide conversion and total charge transfer in the electrocatalytic CBOR. To evaluate the conversion of carbohydrazide in the electrocatalytic CBOR, the AEMFC anode outlet stream was analyzed by HPLC. Additionally, the corresponding cell current was integrated over time to obtain the total charge transferred. In Figure 3 d, the shaded area is equal to the total charge (1.93 C) transferred during electrochemical CBOR, integrated from 3 to 6 min.

For the direct carbohydrazide AEMFC with the metal-catalyst-free 3D graphene anode, the average electron number of electrons transferred per carbohydrazide molecule was 4.9, leading to a 61.3% electron efficiency with respect to complete oxidation of carbohydrazide [Eq. (1)]. The existence of parallel reaction pathways, including both partial and complete oxidation, can thus be confirmed. However, taking into account the electrochemical promotion effect of chemical catalytic reactions ("EPOC"),<sup>[18-20]</sup> the real non-Faradaic reaction rate was likely faster in the electrocatalytic operation than in the control experiment (only carbohydrazide chemical oxidation). Therefore, the actual number of electrons transferred in the electrochemical CBOR should be higher than this apparent value, which strongly suggests that the nanocarbon itself facilitates deep oxidation of carbohydrazide.

After confirming the feasibility of AEMFCs with metal-catalyst-free anode and the corresponding fuel utilization efficiency, a completely metal-catalyst-free direct carbohydrazide AEMFC (Figure 4a) was prepared by combining 3D graphene as the catalyst at the anode, A901 AEM as hydroxide ion conductor in the center, and N-CNT as catalyst for the oxygen reduction reaction at the cathode; and it achieved a PPD of 24.9 mW cm<sup>-2</sup> (Figure 4b). For comparison, a H<sub>2</sub>-AEMFC with nickel-chrome anode catalyst and silver cathode catalyst was developed, generating a PPD of 50 mW cm<sup>-2</sup>.<sup>[6]</sup> Direct alcohol AEMFCs with iron-macrocycle cathode catalysts have also shown promising PPD values.<sup>[21-23]</sup> However, iron, nickel, chrome, or silver metal were still used in the anode and cathode for electro-oxidation of fuels and ORR. Although the PPD is lower than that of platinum-based proton exchange membrane fuel cells, this metal-catalyst-free AEMFC is proposed as one option for a future type of fuel cell. Furthermore, it should be noted that oxygen with 99.99% purity was applied at the cathode in this work. When more ubiquitous CO<sub>2</sub>-containing air is used, a potential concern regarding carbonate precipitation should be considered. This issue could be alleviated by absorbing CO<sub>2</sub> in the air with used anode fuel containing excessive KOH solution. Alternatively, removing liquid KOH from the current fuel cell system is another potential solution.



**Figure 4.** a) Schematic illustration of completely metal-catalyst-free fuel cell. b) Polarization and power density curves of completely metal-catalyst-free direct carbohydrazide AEMFC with 3D graphene anode catalyst (5 mg<sub>catalyst</sub> cm<sup>-2</sup>); AEM: Tokuyama A901; cathode catalyst (1.0 mg<sub>catalyst</sub> cm<sup>-2</sup>); N-CNT; anode fuel: 6.0 M KOH, 1.0 M carbohydrazide,  $4.0 \text{ mLmin}^{-1}$ ; cathode fuel:  $200 \text{ mLmin}^{-1}$  O<sub>2</sub>, ambient pressure; temperature (anode fuel/cathode

In summary, a novel completely metal catalyst-free-direct carbohydrazide AEMFC with a metal-free 3D graphene anode catalyst and an N-CNT cathode catalyst has been successfully developed in this work. These results open a new research arena for exploring the electrocatalytic properties of advanced nanocarbon materials and developing inexpensive fuel cells. Future research efforts, such as modifying the nanocarbon catalysts in order to reduce overpotential, inhibiting non-Faradaic carbohydrazide oxidation reactions, extracting more electrons from the electrocatalytic carbohydrazide oxidation reaction, and minimizing the use of liquid base, should improve the feasibility of current metal-catalyst-free fuel cell technology.

## **Experimental Section**

Experimental details and additional data can be found in the Supporting Information.

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