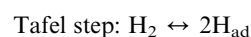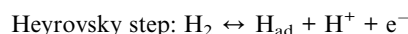## COMMUNICATION

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Nitrogen-doped activated carbon as a metal free catalyst for hydrogen production in microbial electrolysis cells†

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Nitrogen-doped activated carbon was investigated as an alternative cathode catalyst for hydrogen production in microbial electrolysis cells (MECs). Both electrochemical and MEC tests confirmed that nitrogen doping was an effective method in improving the catalytic activity of activated carbon towards the hydrogen evolution reaction (HER). This improvement was attributed to the increased nitrogen content in activated carbon, as a higher content of nitrogen would facilitate the Volmer step in HER. Although the overall performance of the nitrogen-doped activated carbon was lower than the platinum-based catalysts, its low cost and (potentially) long-term stability would compensate for a low hydrogen production rate.

1. Introduction

A microbial electrolysis cell (MEC) is an electrochemical device that produces hydrogen gas with the help of electrochemically-active bacteria.[1] In a typical MEC, the anodic bacteria utilize the anode as an electron acceptor during metabolism of organic matter present in wastewater. The electrons released from the oxidation process travel through an external circuit to a cathode electrode, which reduces protons to hydrogen gas. An external voltage >0.2 V is usually required to overcome the thermodynamic barrier for the hydrogen evolution reaction (HER).[2]

HER requires the aid of catalysts, and the most widely used HER catalyst in MEC is platinum (Pt). However, due to the scarcity and high cost of Pt, it is not economically feasible to use Pt-based catalysts in large-scale MEC systems for deployment in wastewater treatment.[3] Therefore, the search for alternative and

low cost cathode HER catalyst is one of the most important tasks that must be addressed towards MEC development.[4] Indeed, various alternative cathode HER catalysts have been examined in MECs.[4,5] However, the congeners of Pt, such as Pd[6] and Ni[7] are still costly for wastewater treatment application, and the compounds of other metals, such as MoS_2[8,9] and nano-structured iron,[10] lack the stability and usually involve a complex procedure of preparation.

It is well documented that the HER involves several independent steps:[11]

$$\text{Volmer step: } H_{ad} \leftrightarrow H^+ + e^-$$

$$\text{Heyrovsky step: } H_2 \leftrightarrow H_{ad} + H^+ + e^-$$

$$\text{Tafel step: } H_2 \leftrightarrow 2H_{ad}$$

It has been confirmed theoretically that the nitrogen doping would increase the electron densities in some of the adjacent carbon atoms and make them more readily to donate electrons.[12] Therefore, it is reasonable to expect that the chemisorption of H^+, *i.e.*, the Volmer step of hydrogen generation, could be accelerated if nitrogen doped carbon materials are used as a catalyst for HER. However, on the other hand, the enhanced stability of H_{ad} formed may in turn inhibit the following steps in the hydrogen generation. Thus, it is worth investigating whether nitrogen doping is a feasible method that can effectively enhance the catalytic activity of carbon materials in catalyzing the hydrogen production.

Previously, we have shown that nitrogen doping could significantly increase the catalytic activity of activated carbon (AC) towards oxygen reduction reaction.[13] Because AC is commercially available in bulk quantity at a relatively low price, it has been widely used in water treatment[14] and wastewater treatment processes.[15] However, to our best knowledge, there have not been any studies of examining AC or its derivatives for hydrogen generation in an MEC. In this study, we have evaluated the nitrogen doped AC (AC_N) as a metal-free catalyst for

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hydrogen production in both electrochemical cells and MECs, and compared its performance with the Pt-based catalysts and pristine AC.

2.   Methods and materials

2.1   The preparation of the catalyst

The AC_N was synthesized according to the methods described in our previous work.[13] The commercially available activated carbon (Fisher Scientific, Bridgewater, NJ, USA) was used as a base material. To better facilitate the nitrogen doping process, the AC was sequentially treated with acidic and alkaline solutions. During the acidic pretreatment process, two grams of AC powder was added into a solution containing 25 mL of H_2SO_4 (98%) and 2 grams of $KMnO_4$, and mixed for 3 hours. Then, the acid treated AC was washed thoroughly using DI water. After that, the acid pretreated AC was further treated in a 3 M KOH solution at 180 °C for 10 hours; the acid–alkaline pretreated AC was then thoroughly washed with DI water and used in the following nitrogen doping.

A solid state nitrogen precursor, cyanamide (Sigma-Aldrich, St. Louis, MO, USA), was used as a nitrogen source for nitrogen doping. The acid–alkaline pretreated AC and the cyanamide powder were mixed in 1 : 5 (mass ratio) and loaded into a programmable tube furnace (Lindberg, Thermo Scientific, USA). The tube furnace was flushed with argon gas for 10 min before the doping to ensure an inert atmosphere. During the doping process, the tube was flushed with argon gas at a flow rate of 0.1 mL s^{-1} continuously. The temperature of the furnace was increased from the room temperature to 80 °C in 10 min and maintained at 80 °C for 1 h; then the temperature was further increased to 750 °C in 4 h and maintained at 750 °C for additional 2 h.

2.2   Electrochemical characterization

Linear sweep voltammetry (LSV) was conducted to evaluate the electrochemical property of AC and AC_N using a potentiostat (CH Instrument 600D, Austin, TX, USA). The LSV was scanned from 0 V to −1.5 V under a scan rate of 50 mV S^{-1}. The electrochemical cell used in the experiment had a standard three-electrode setup, in which the glassy carbon electrode was used as a working electrode, with a Pt wire and a Ag/AgCl electrode (+0.197 mV) as a counter electrode and a reference electrode, respectively. To better understand the process of hydrogen generation on the catalysts, three different electrolytes with different pH values were used, including 0.5 M H_2SO_4, 100 mM PBS (phosphate buffer solution) and 1 M NaOH. The 100 mM PBS solution contains (per L): K_2HPO_4, 10.7 g; and KH_2PO_4, 5.3 g. The catalyst ink was prepared by dissolving 5 mg of catalysts (AC or AC_N) in 500 μL of Nafion solution (Sigma-Aldrich, St. Louis, MO, USA). An aliquot of 5 μL of the ink was pipetted on top of the polished glassy carbon electrode and dried at room temperature before use.

2.3   MEC setup and operation

A flat plate MEC reactor was built to study the performance of the prepared HER catalysts for hydrogen production. The anode chamber and the cathode chamber of the MEC had the same working volume, which was 30 mL. The anode chamber and cathode chamber were separated by a piece of cation exchange membrane (Membrane International, Inc., NJ, USA). The anode electrode was a 5 cm long carbon brush and the anode was inoculated with digester effluent from Southshore wastewater treatment plant (Milwaukee, WI, USA). The cathode electrode was a piece of carbon cloth (3 cm × 5 cm) on which the catalysts were loaded using Nafion solution as previously described.[10,16] The catalyst loading rate on the cathode electrode was 5 mg cm^{-2}. A titanium wire was used as a current collector to connect the cathode electrode to an external circuit that consisted of a DC power supply, which was set at 0.8 V throughout the experiment, and a 1 Ω resistor. The hydrogen gas produced was collected in a graduated cylinder by water replacement. The anode solution contains (per L of tap water): sodium acetate, 1 g; NH_4Cl, 0.15 g; NaCl, 0.5 g; $MgSO_4$, 0.015 g; $CaCl_2$, 0.02 g; KH_2PO_4, 0.53 g; K_2HPO_4, 1.07 g; yeast extract, 0.1 g; and trace element, 1 mL.[17] The cathode solution contains (per L of tap water): K_2HPO_4, 10.7 g; and KH_2PO_4, 5.3 g. At the beginning of each cycle, 200 mL of fresh anode solution was added into a reservoir and recirculated through the anode chamber at a flow rate of 30 mL min^{-1}, while the catholyte was replaced as well but without mixing. The voltage across the resistor was recorded every 5 min using a data acquisition system (Model 2700, Keithley Instruments, Cleveland, OH, USA).

3.   Results and discussions

3.1   Electrochemical performance of AC_N

The morphology of the synthesized AC_N did not show noticeable changes according to SEM (ESI†). Fig. 1 presents the LSV curves for the pristine AC and the AC_N electrodes in acidic, neutral, and alkaline electrolyte, respectively. One can observe that the AC_N shows a significantly improved performance for HER in terms of overpotential and current density compared with the pristine AC. The AC_N exhibited an onset potential at *ca.* −0.9 V in 100 mM PBS (pH = 7), −0.8 V in 0.5 M H_2SO_4 (pH = 0), and −1.0 V in 1 M NaOH (pH = 14) of AC, respectively, showing a distinct positive shift relative to the pristine AC, which had an onset potential at −1.0 V in 100 mM PBS (pH = 7), −0.9 V in 0.5 M H_2SO_4 (pH = 0), and −1.2 V in 1 M NaOH (pH = 14). In addition, the AC_N also showed a higher current density of HER than the pristine AC under the same potential, confirming our hypothesis that nitrogen doping could enhance the catalytic activity of AC towards hydrogen production.

The nitrogen doping treatment encourages the formation of H_{ad} from H^+ and this would have two implications during the hydrogen generation. First, the formation of H_{ad} could be more favored and thus facilitate the Volmer step. Second, the facilitated formation of H_{ad} might impede the Heyrovsky step and Tafel step, as H_{ad} was an reactant in these two steps. However, according to the LSV result, the onset potentials for the HER of
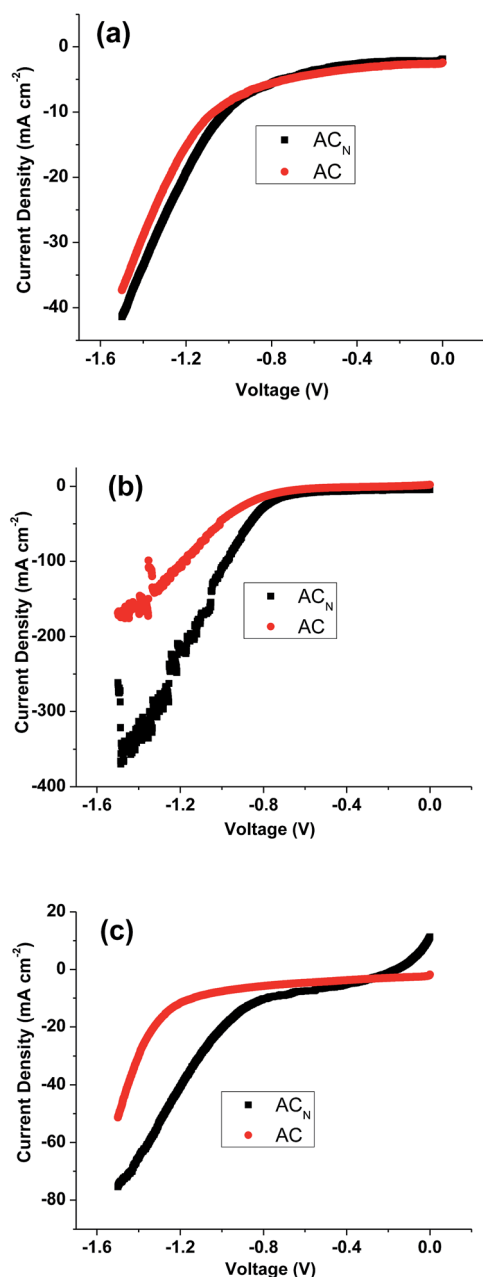
Fig. 1 The LSV tests of AC_N and AC: (a) in 100 mM PBS buffer solution, (b) CV in 0.5 M H_2SO_4 solution, and (c) CV in 1 M NaOH solution.

AC_N were consistently more positive than that of pristine AC in the three electrolytes tested, indicating that the overall effect of nitrogen doping reduced the thermodynamic barrier of hydrogen formation, *i.e.*, the contribution of nitrogen doping towards the Volmer step outweighed its negative impacts on the Heyrovsky step and the Tafel step. Moreover, the increased catalytic activity of AC_N was more pronounced in the NaOH solution. One possible explanation is that the Volmer step ($H_{ad} \leftrightarrow H^+ + e^-$) was not limited by the H^+ that was largely available in the H_2SO_4 or PBS solution; however, when the electrolyte was changed to the basic solution, the concentration of H^+ became so low that the adsorption of H^+ on the surface of AC was the

rate limiting step, and in this case, an extra energy barrier would have to be overcome so that the HER could proceed. Because AC_N had increased capacity in forming H_{ad}, the impact of low H^+ concentration on the Volmer step was less significant for AC_N, compared with pristine AC. The feature of enhanced formation of H_{ad} on AC_N is of practical importance in MEC operation. In a two chamber MEC, the catholyte pH increases as hydrogen gas is produced. Thus, an HER catalyst that can operate at high pH with low extra thermodynamic barrier will allow less frequent replacement of the catholyte or less buffer use, which will translate into lower operational cost for MECs.

Table 1 summarizes the potentials at which the cathodic currents reached 10 mA cm^{-2} in the different electrolytes. The AC_N consistently exhibited better kinetic performances in catalyzing hydrogen production compared to pristine AC. The potentials needed for the AC_N cathode to reach 10 mA cm^{-2} were lower than those needed for the pristine AC cathode in all the three electrolytes tested. Furthermore, this difference in potentials was more pronounced in NaOH solution than the other two electrolytes, which further confirmed our hypothesis that the nitrogen doping could potentially facilitate the Volmer step and the overall HER reaction. It should be noted that the ionic strengths of H_2SO_4 and NaOH solutions were much higher than that of PBS solution, thus more negative potentials were required for the AC_N and AC cathodes to reach the same current density (10 mA cm^{-2}) than in H_2SO_4 and NaOH solutions; however, this should not be interpreted as hydrogen production was least kinetically favored in a neutral solution.

3.2 MEC performance

The current generation of the MEC with different cathode catalysts is shown in Fig. 2. Among the three catalysts tested, the MEC with the AC_N cathode achieved higher current densities than the one with the AC cathode. The peak current densities of AC_N and AC were 0.48 $\pm$ 0.02 mA cm^{-2} and 0.33 $\pm$ 0.03 mA cm^{-2}, respectively. This was consistent with the trend obtained in the LSV test. More remarkably, the current density of AC_N was even comparable to that of Pt/C (0.42 $\pm$ 0.04 mA cm^{-2}). These results further confirmed that nitrogen doping was an effective approach to enhance the catalytic activity of AC for hydrogen generation.

The rate of the hydrogen gas produced over multiple operating cycles with different catalysts is presented in Fig. 3. The hydrogen generation rates for the AC_N cathode and the AC cathode were 0.0030 $\pm$ 0.0004 m^3 per m^2 per day (normalized by the projected cathode area) and 0.0014 $\pm$ 0.0010 m^3 per m^2 per day, respectively. Using *T*-test analysis, we confirmed that the MEC with the AC_N cathode produced two times of hydrogen gas

Table 1 A list of the potentials (in volts *vs.* Ag/AgCl) at which the cathodic current densities reached 10 mA cm^{-2}

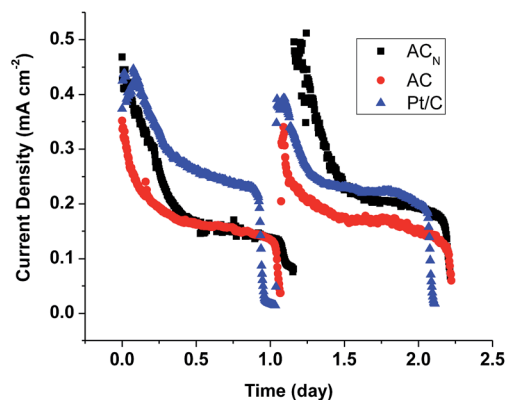|	AC_N	Pristine AC
PBS	−1.016	−1.070
H_2SO_4	−0.625	−0.750
NaOH	−0.782	−1.139

Fig. 2 Current generation in the MEC with different HER catalysts including Pt/C, AC_N and raw AC.
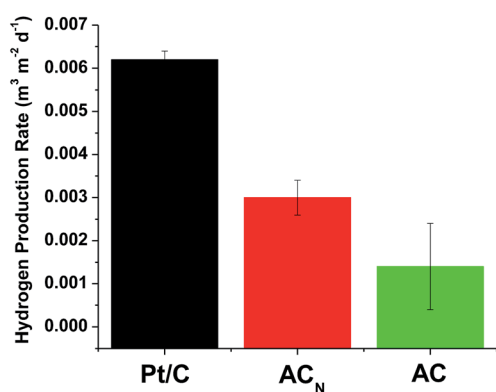

Fig. 3 The hydrogen gas production rate (normalized to the cathode chamber volume) from MEC with different catalysts.

than the one with the AC cathode ($p < 0.05$). In addition, the cathodic efficiency of the AC_N cathode ($12.25 \pm 1.07\%$) was also much higher than that of AC cathode ($7.80 \pm 4.06\%$). Higher hydrogen production rate and cathodic efficiency of AC_N provided further evidence that nitrogen doping was an effective method to improve the AC catalytic activity for hydrogen production in MECs.

Although the MEC with the AC_N cathode generated similar current densities to the one with the Pt/C cathode, the AC_N cathode produced only half the amount of hydrogen gas that the Pt/C cathode produced in MEC (Fig. 3), which was 0.0060 ± 0.0002 m^3 per m^2 per day. This discrepancy should be attributed to better cathodic efficiency of the Pt/C, in terms of selective reduction of the target reactants and less energy consumption by catalytic process, both of which require further investigation. Based on the current generation and the hydrogen gas produced, the cathodic efficiency for Pt/C and AC_N were $23.11 \pm 1.30\%$ and $12.25 \pm 1.07\%$, respectively. Thus, the Pt-based catalysts are still superior in catalyzing HER. However, considering that the cost of as synthesized AC_N was only 1/6 of the cost of commercial Pt/C and that this cost could be further lowered by using cheaper nitrogen precursor,[13] the AC_N could be a promising alternative HER catalyst to Pt/C in larger scale MECs.

4.   Conclusions

In this study, we have demonstrated that the nitrogen doping process could increase the capability of AC for hydrogen evolution reaction. The nitrogen doping enhanced the formation of H_{ad} on AC, which facilitated the Volmer step, and reduced the energy barrier for hydrogen generation, especially under a high pH situation. When being employed in an MEC as a cathode catalyst, both the hydrogen production and cathodic efficiency of AC_N were higher than those of pristine AC. The increased catalytic activity together with the low cost of AC_N makes it a promising HER catalyst. Future research will need to further reduce the cost of AC_N through optimizing the doping procedure and using cheaper nitrogen precursors, and to examine its stability for long-term operation of MECs.

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