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2012

Seyed, A. M. S., Nguyen, N. T., Seyyed, M. M. E., & Chan, S. H. (2012). A membraneless hydrogen peroxide fuel cell using Prussian Blue as cathode material. *Energy & Environmental Science*, 5(8), 8225-8228.

<https://hdl.handle.net/10356/93947>

<https://doi.org/10.1039/C2EE21806B>

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Cite this: DOI: 10.1039/c0xx00000x

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Membraneless hydrogen peroxide fuel cell using Prussian Blue as cathode material†

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DOI: 10.1039/b000000x

This communication describes the exploitation of Prussian Blue, ferric ferrocyanide ($\text{Fe}_4^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3$), for the cathode side in a single-chamber membraneless fuel cell running on hydrogen peroxide (H_2O_2) as both fuel and oxidant. An open-circuit voltage (OCV) of 0.6 V has been obtained, which could be the highest OCV with H_2O_2 ever reported. The maximum power density was 1.55 mW cm^{-2} which showed a stable long-term operation in acidic media.

Environment-friendly technologies for energy supply, storage and conversion are the challenges of twenty first century and need long-term fundamental innovative research.^{1,2} Ideally, such technologies must be able to convert plentiful energy-poor molecules into energy-rich molecules using renewable energies, mainly sunlight, with highly active but cheap and abundant catalyst materials.³

Interestingly, hydrogen peroxide is a carbon-free energy carrier that can be used as both fuel and oxidant in a fuel cell engine. The whole fuel cell system would have advantages of a simple design.^{4,5} Hydrogen peroxide has high energy density and decomposes into water and oxygen.⁶ This compound is fairly nontoxic, and can be easily transported in the aqueous phase.⁶ Electricity generated by a photovoltaic solar cell can be used for hydrogen peroxide production through electrocatalytic reduction of oxygen in an acidic aqueous solution.⁵

In order to use hydrogen peroxide as both fuel and oxidant, it can be exploited in basic and acidic supporting electrolytes representing the fuel (electron donor) and the oxidant (electron acceptor), respectively. In such a basic–acidic bipolar electrolytes configuration, the fuel and oxidant should be kept separate in a membrane-based design⁷ or in a microfluidic channel⁸ where diffusive mixing is limited to a confined liquid–liquid interface. Using 1 M H_2O_2 in a 6 M KOH solution as a fuel and 2 M H_2O_2 in a 1.5 M H_2SO_4 solution with Ni/C and Pt/C as catalysts at anode and cathode sides in a Nafion-membrane fuel cell, a power density of 3.75 mW cm^{-2} at a cell potential of 0.55 V was achieved.⁷ In a microfluidic cell running on 0.75 M H_2O_2 with NaOH/ H_2SO_4 electrolytes at a flow rate of 24 $\mu\text{L s}^{-1}$ using Pt electrodes, a maximum power density of 23 mW cm^{-2} at a cell potential of 0.3 V was obtained.⁸

There are few standing issues for such alkaline–acidic bipolar electrolytes. First, there is a mismatch between the supporting

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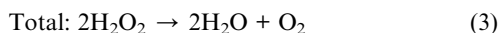
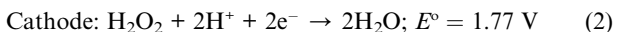
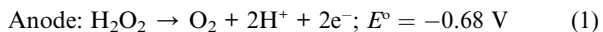
† Electronic supplementary information (ESI) available. See DOI: 10.1039/c2ee21806b

Broader context

Hydrogen peroxide is a carbon-free energy carrier which promises a sustainable energy system. Hydrogen peroxide can be produced using electricity generated by a solar cell, while chemical energy stored in hydrogen peroxide can be converted into electric power in a fuel cell with oxygen and water as byproducts. The whole process is environment-friendly. Hydrogen peroxide can be used as both fuel and oxidant in a single-compartment membraneless fuel cell to make a fully green power engine. This fuel cell configuration has inherent simplicity in design, integration and operation requirements. Design and development of selective and economically viable catalysts for efficient oxidation and reduction of hydrogen peroxide in a single compartment is of great importance. On the one hand, efficient catalysts should facilitate the electrochemical reactions over the electrodes. On the other hand, they must have low catalytic reactivity for hydrogen peroxide decomposition. A membraneless hydrogen peroxide fuel cell does not suffer from standing problems of the membrane electrode assembly (MEA) observed in conventional membrane-based fuel cells. Consequently, a single-compartment hydrogen-peroxide-based fuel cell is a suitable power source for portable and miniaturized applications. The design reported here can be used for making “on-chip fuel cells” or “micro-fuel cells” for powering a wide range of micro-devices, including micro-robots, submarine sensors and point-of-care portable medical devices.

electrolytes of the anolyte and the catholyte. Second, using noble metals such as platinum, Pt, is certainly efficient for the reduction of H_2O_2 to water. But concurrently, they also facilitate the direct decomposition of H_2O_2 to oxygen.⁷⁻⁹ In addition, the exothermic neutralization of H^+ and OH^- may happen because of the diffusive mixing of the reactants resulting in a consequent electrolyte consumption.¹⁰

To address the above mentioned issues, H_2O_2 can be used in a one-compartment fuel cell with electrodes of different reactivity to oxidation and reduction of H_2O_2 which is given by:^{5,11}



The theoretical electromotive force for the reactions is 1.09 V which is comparable to the theoretical open-circuit voltage (OCV) of a hydrogen-oxygen fuel cell (1.23 V) and a direct methanol fuel cell (1.21 V).

Yamazaki *et al.*⁴ developed an alkaline one-compartment fuel cell with a maximum open-circuit potential of 0.13 V using Pt, Pd, Ni and Au wires as a selective anode and an Ag wire as a selective cathode. Yamada *et al.*⁵ improved the OCV of an alkaline fuel cell to 0.16 V using Ag-Pb alloy nanoparticles as a cathode with higher surface area and improved reactivity due to the combination with an Au anode.

In a recent work, Yamada *et al.*¹¹ developed an acidic one-compartment fuel cell using an iron phthalocyanine complex as a cathode and a Ni mesh as an anode. Using $[\text{Fe}^{\text{III}}(\text{Pc})\text{Cl}]$ as a cathode material in an acetate buffer containing 300 mM H_2O_2 with pH of 3, an OCV of 0.5 V with a maximum power density of $10 \mu\text{W cm}^{-2}$ and a limiting current density of $210 \mu\text{A cm}^{-2}$ were achieved. Since H_2O_2 is produced under acidic environment *via* the two-electron reduction of O_2 using solar power,⁵ operation under acidic conditions is highly desirable in order to establish a hydrogen peroxide-based energy production and storage.

In this communication, we report a one-compartment fuel cell running on H_2O_2 as both fuel and oxidant under acidic conditions. Prussian Blue coated on carbon-fiber-based paper was used at the cathode side while the anode was made of silver foil (Ag) or a nickel

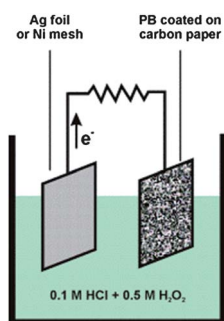


Fig. 1 A schematic figure of a one-compartment fuel cell running on H_2O_2 as both fuel and oxidant. Supporting electrolyte is 0.1 M HCl dissolved in 0.5 M H_2O_2 . The anode consists of either a silver foil or a nickel mesh. The cathode is made of Prussian Blue coated on carbon paper.

mesh (Ni), Fig. 1. Prussian Blue or ferric ferrocyanide ($\text{Fe}_4^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3$) is widely available and very cost effective compared to precious metals.¹² Prussian Blue (PB) is a renowned catalyst for H_2O_2 reduction under acidic conditions and its electrocatalytic reduction of hydrogen peroxide for biosensing and analytical applications has been studied extensively.^{12,13}

The procedure of chemical preparation of PB was adopted from elsewhere.⁹ Briefly, PB was synthesized chemically by mixing of 0.5 M FeCl_3 in 0.1 M HCl with a solution of $\text{K}_3[\text{Fe}(\text{CN})_6]$ in 0.1 M HCl at room temperature. To make PB supported on carbon, the required amount of Vulcan XC-72 was suspended in 0.1 M HCl. $\text{K}_3[\text{Fe}(\text{CN})_6]$ in 0.1 M HCl and 0.5 M FeCl_3 in 0.1 M HCl were then added drop wise to the carbon slurry, respectively (please refer to ESI† for catalyst preparation, characterization and electrode fabrication). Both unsupported and carbon-supported synthesized PB were analyzed using the powder X-ray diffraction (XRD) technique. Fig. 2 shows pronounced peaks at $2\theta = 17.4$, $2\theta = 24.6$, $2\theta = 35.2$ and $2\theta = 39.4$ corresponding to $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$ (ref. 9). The XRD peaks for both carbon-supported and unsupported PB remained identical indicating that the modification process has no effect on the crystallinity of PB. There was also no reaction between PB and carbon.

The electrocatalytic reduction of H_2O_2 over PB was examined in a three-electrode cell with a rotating ring-disk glassy carbon electrode. Small portions of unsupported and carbon-supported PB solution containing Nafion (2 μL) were placed on the glassy carbon electrode. Fig. 3 shows the cyclic voltammetry (CV) results of H_2O_2 on a glassy carbon electrode modified by unsupported PB in a supporting electrolyte of 0.1 M HCl (pH = 1) containing 0.5 M H_2O_2 . It is worth mentioning that many large fluctuations and asperities were observed while conducting cyclic voltammetry of the carbon-supported PB in the presence of H_2O_2 , which are likely due to the limitation of H_2O_2 transport to the electrode. Rapid emergence of bubbles, even at a high rotating speed of 2500 rpm, was observed over the glassy carbon modified by carbon-supported PB. Since the cathodic

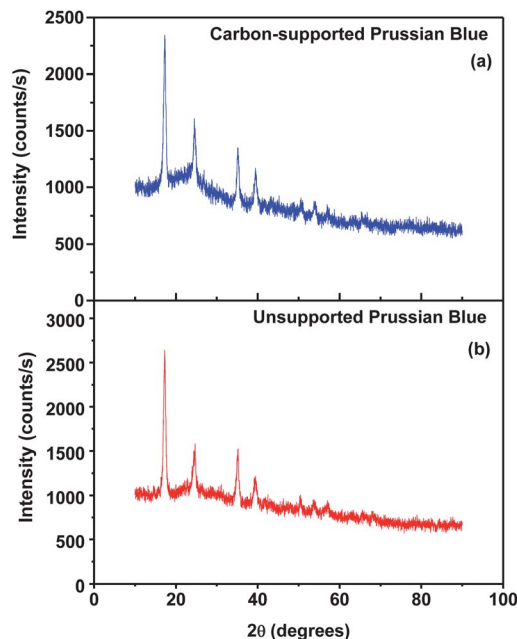


Fig. 2 Powder X-ray diffraction (XRD) patterns for (a) carbon-supported and (b) unsupported Prussian Blue.

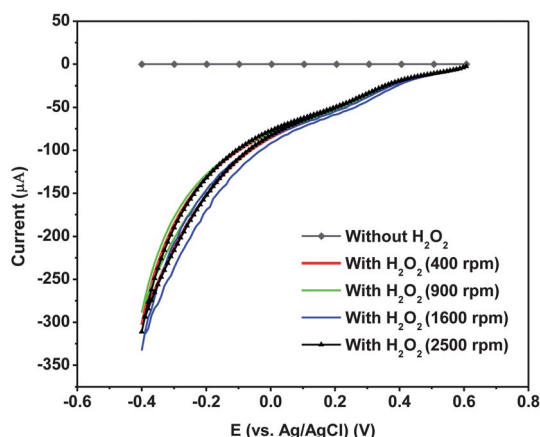


Fig. 3 Cyclic voltammograms of H_2O_2 on a glassy carbon electrode modified by unsupported PB. The measurements were performed in an aqueous electrolyte of 0.1 M HCl containing 0.5 M H_2O_2 . Scan rate of 10 mV s^{-1} was selected.

reaction (2) does not liberate any gases, bubble generation is associated with H_2O_2 decomposition reaction.

The cyclic voltammogram of the unsupported PB in the 0.5 M HCl solution in the absence of H_2O_2 indicates that there is no specific catalytic current of H_2O_2 reduction in the cathodic sweep.

As shown in Fig. 3, cyclic voltammograms of the unsupported PB in the presence of H_2O_2 show the onset potential for H_2O_2 reduction on the glassy carbon electrode with PB as 0.6 V. In order to have selective electrodes, the onset potential for H_2O_2 oxidation on an electrode of interest should be lower than the onset potential for H_2O_2 reduction over PB. As a case study, the onset potential for H_2O_2 oxidation on a nickel (Ni) electrode and on a silver (Ag) electrode in an alkaline medium are *ca.* -0.09 V and *ca.* -0.11 V (ref. 4), respectively. Both potentials are lower than 0.6 V. Therefore, Ni and Ag electrodes were selected as potential anodes for the fuel cell. Since PB is not stable under alkaline conditions, the selectivity of Ni and Ag electrodes compared to PB were examined in a fuel cell with an acidic medium.

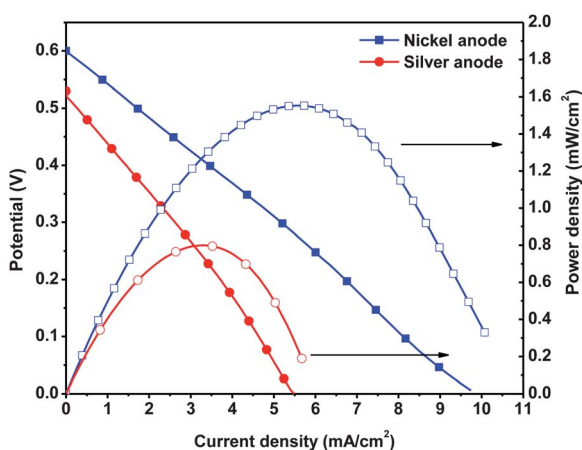


Fig. 4 Current-potential and current-power curves of the single-compartment H_2O_2 fuel cell with nickel and silver anodes and unsupported PB coated on carbon paper as a cathode. Performance tests were carried out under acidic conditions using 0.1 M HCl and 0.5 M H_2O_2 .

PB-coated electrodes were prepared by spraying a solution of PB containing Nafion® on a piece of carbon paper. The silver anode was made of a thin silver plate from Sigma-Aldrich while the nickel anode was a metallic mesh. The anode and cathode were immersed in a solution of 0.5 M H_2O_2 with a supporting electrolyte of 0.1 M HCl.

Linear potential sweep voltammetry was carried out to examine the potential-current characteristics of the single-compartment fuel cell. Fig. 4 shows that the fuel cell has a high open circuit potential of 0.53 V and 0.6 V using silver and nickel anodes, respectively. In addition, a maximum power density of *ca.* 0.8 mW cm^{-2} at 0.3 V with a silver anode and a maximum power density of *ca.* 1.55 mW cm^{-2} at 0.3 V with a nickel anode were observed. These results are two orders of magnitude higher than the best results reported in the literature, which was $10 \mu\text{W cm}^{-2}$ (ref. 11). In addition, the PB coated on carbon paper was very stable under acidic conditions. These conditions are compatible with the production of H_2O_2 through the electrochemical two-electron reduction of O_2 (ref. 5).

Conclusions

A high performance membraneless H_2O_2 fuel cell using Prussian Blue as cathode and silver and nickel as anode materials in an acidic medium was realized. Open-circuit potential and maximum power density are improved significantly compared to the past results reported in the literature. The current design provides a strong platform for further developments. Prussian Blue is highly stable in an acidic environment with high electroactivity towards the reduction of H_2O_2 , consequently other materials can be explored for lower anode overpotential (see ESI†). Since carbon-supported Prussian Blue facilitated the spontaneous decomposition of H_2O_2 , other support materials should be explored in the future.

In addition, the current fuel cell design is very suitable for on-chip power generation schemes such as powering portable lab-on-chip devices¹⁴ and off-the grid micro-sensors.^{15,16} Fuel crossover and mixing of fuel and oxidant is not an issue for this concept. Unlike microfluidic fuel cells, continuous streams of the fuel and oxidant are not required to keep the fuel separated from the oxidant.¹⁷ Compared to other on-chip power sources,¹⁴⁻¹⁶ the fuel cell reported here has a simple design without a membrane electrode assembly (MEA), a superior performance and easy fuel-oxidant handling. These features allow the fuel cell to be integrated with other microdevices for portable applications.

Acknowledgements

The authors would like to thank Assistant Professor Chee-Seng Toh and Lai Peng Wong from School of Physical and Mathematical Sciences, and Dr Lan Zhang from the School of Mechanical and Aerospace Engineering, Nanyang Technological University for their valuable comments.

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