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

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This communication describes the exploitation of Prussian Blue, ferric ferrocyanide (Fe₄[Fe₆(CN)₆])₄\(^{1}\) for cathode side in a single-chamber membraneless fuel cell running on hydrogen peroxide (H₂O₂) as both fuel and oxidant. An open-circuit potential (OCP) of 0.6 V has been obtained, which could be the highest OCP with H₂O₂ ever reported. The maximum power density was 1.55 mW/cm² and 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 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\(^{7}\).

In order to use hydrogen peroxide as both fuel and oxidant, hydrogen peroxide can be exploited in basic and acidic supporting electrolytes representing fuel (electron donor) and oxidant (electron acceptor), respectively. In such a basic/acidic bipolar electrolyte configuration, fuel and oxidant should be kept separate in a membrane-based design\(^{7}\) or in a microfluidic channel\(^{8}\) where diffusive mixing is limited to a confined liquid-liquid interface. Using 1 M H₂O₂ in a 6 M KOH solution as fuel and 2 M H₂O₂ in a 1.5 M H₂SO₄ 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/cm² at a cell potential of 0.55 V was achieved\(^{7}\). In a microfluidic cell running on 0.75 M H₂O₂ with NaOH/H₂SO₄ electrolytes at a flow rate of 24 µL/s using Pt electrodes, a maximum power density of 23 mW/cm² at cell potential of 0.3 V was obtained\(^{4}\).

There are few standing issues for such alkaline/acidic bipolar electrolytes. First, there is a mismatch between the supporting electrolytes of the anolyte and the catholyte. Second, using noble metals such as platinum Pt is certainly efficient for the reduction of H₂O₂ to water. But concurrently, they also facilitate the direct decomposition of H₂O₂ 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, H₂O₂ can be used in a one-compartment fuel cell with electrodes of different reactivity to oxidation and reduction of H₂O₂ given by\(^{5,11}\):

Anode: H₂O₂ → O₂ + 2H⁺ + 2e⁻ E’ = 0.68 V (1)
Cathode: H₂O₂ + 2H⁺ + 2e⁻ → 2H₂O E’ = 1.77 V (2)
Total: 2H₂O₂ → 2H₂O + O₂ (3)

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

In a recent work, Yamada 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 selective anode and Ag wire as selective cathode. Yamada et al.\(^{3}\) improved the OCV of an alkaline fuel cell to 0.16 V using Ag-Pb alloy nanoparticles as cathode with higher surface area and improved reactivity due to the combination with an Au anode.

In this communication, we report a one-compartment fuel cell running on H₂O₂ as both fuel and oxidant under acidic conditions. Prussian Blue coated on carbon-fiber-based paper was used at the cathode side while anode was made of silver foil (Ag) or nickel mesh (Ni), Figure 1. Prussian Blue or ferric ferrocyanide (Fe₄[Fe₆(CN)₆])₄ is widely available and very cost effective compared to precious metals. Prussian Blue (PB) is a renowned...
catalyst for \( \text{H}_2\text{O}_2 \) reduction under acidic conditions and its electrocatalytic reduction of hydrogen peroxide for biosensing and analytical applications has been studied extensively.\(^{12, 13}\)

Fig. 1. A schematic figure of one-compartment fuel cell running on \( \text{H}_2\text{O}_2 \) as both fuel and oxidant. Supporting electrolyte is 0.1 M HCl dissolved in 0.5 M \( \text{H}_2\text{O}_2 \). The anode consists of either a silver foil or a nickel mesh. The cathode is made of Prussian Blue coated on carbon paper.

The procedure of chemical preparation of PB was adopted from elsewhere.\(^{9}\) Briefly, PB was synthesized chemically by mixing of 0.5 M \( \text{FeCl}_3 \) in 0.1 M HCl with a solution of \( \text{K}_3\text{[Fe(CN)]}_6 \) 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 and 0.5 M \( \text{FeCl}_3 \) 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 powder X-ray diffraction (XRD) technique. Figure 2 shows pronounced peaks at \( 2\theta=17.4, 20=24.6, 20=35.2 \) and \( 20=39.4 \) corresponding to \( \text{Fe}_6\text{[Fe(CN)]}_9 \), \( \text{xH}_2\text{O} \). 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 \( \text{H}_2\text{O}_2 \) 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 \( \mu \)l) were placed on the glassy carbon electrode. Figure 3 shows the cyclic voltammetry (CV) results of \( \text{H}_2\text{O}_2 \) on a glassy carbon electrode modified by unsupported PB in a supporting electrolyte of 0.1 M HCl (pH=1) containing 0.5 M \( \text{H}_2\text{O}_2 \). 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 \( \text{H}_2\text{O}_2 \), which are likely due to the limitation of \( \text{H}_2\text{O}_2 \) transport to the electrode. Rapid emergence of bubbles, even at high rotating speed of 2500 rpm, was observed over the glassy carbon modified by carbon-supported PB. Since the cathodic reaction (2) does not liberate any gases, bubble generation is associated with \( \text{H}_2\text{O}_2 \) decomposition reaction.

Cyclic voltammogram of the unsupported PB in the 0.5 M HCl solution in the absence of \( \text{H}_2\text{O}_2 \) indicates that there is no specific catalytic current of \( \text{H}_2\text{O}_2 \) reduction in the cathodic sweep.

As shown in Figure 3, cyclic voltammograms of the unsupported PB in the presence of \( \text{H}_2\text{O}_2 \) show the onset potential for \( \text{H}_2\text{O}_2 \) reduction on the glassy carbon electrode with PB is 0.6 V. In order to have selective electrodes, the onset potential for \( \text{H}_2\text{O}_2 \) oxidation on an electrode of interest should be lower than the onset potential for \( \text{H}_2\text{O}_2 \) reduction over PB. As a case study, the onset potential for \( \text{H}_2\text{O}_2 \) oxidation on a nickel (Ni) electrode and on a silver (Ag) electrode in alkaline medium are ca. -0.09 V and ca. -0.11 V, 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 in alkaline conditions, the selectivity of Ni and Ag electrodes compared to PB were
examined in a fuel cell with acidic medium.

PB-coated electrodes were prepared by spraying a solution of PB containing Nafion® on a piece of carbon paper. Silver anode was made of a thin silver plate from Sigma-Aldrich while nickel anode was a metallic mesh. Anode and cathode were immersed in a solution of 0.5 M H₂O₂ 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. Figure 4 shows that the fuel cell has a high open circuit potential of 0.53 V and 0.6 V using silver and nickel anode, respectively. In addition, a maximum power density of ca. 0.8 mW/cm² at 0.3 V with a silver anode and a maximum power density of ca. 1.55 mW/cm² 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 μW/cm². In addition, the PB coated on carbon paper was very stable under acidic condition. This condition is compatible with the production of H₂O₂ through the electrochemical two-electron reduction of O₂.

![Diagram](image)

**Fig. 4.** Current-potential and current-power curves of the single-compartment H₂O₂ fuel cell with nickel and silver anodes and unsupported PB coated on carbon paper as cathode. Performance tests were carried out under acidic condition using 0.1 M HCl and 0.5 M H₂O₂.

**Conclusions**

A high performance membraneless H₂O₂ 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 is 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 acidic environment with high electroactivity towards the reduction of H₂O₂, consequently other materials can be explored for lower anode overpotential (see ESI†). Since carbon-supported Prussian Blue facilitated the spontaneous decomposition of H₂O₂, 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 devices and off-the-grid micro sensors. Fuel crossover and mixing of fuel and oxidant is not an issue for this concept. Unlike microfluidic fuel cells, continuous streams of fuel and oxidant are not required to keep fuel separated from oxidant.

Compared to other on-chip power sources, 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.

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**Notes and references**