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Photoregenerative I$^-$/I$_3^-$ couple as a liquid cathode for proton exchange membrane fuel cell

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A photoassisted oxygen reduction reaction (ORR) through I$^-$/I$_3^-$ redox couple was investigated for proton exchange membrane (PEM) fuel cell cathode reaction. The I$^-$/I$_3^-$-based liquid cathode was used to replace conventional oxygen cathode, and its discharge product I$^-$ was regenerated to I$_3^-$ by photocatalytic oxidation with the participation of oxygen. This new and innovative approach may provide a strategy to eliminate the usage of challenging ORR electrocatalysts, resulting in an avenue for developing low-cost and high-efficiency PEM fuel cells.

The complex oxygen reduction reaction (ORR) in the proton exchange membrane fuel cells (PEMFC) significantly affects their performance. On the one hand, the complex ORR process requires expensive noble metal catalysts to improve the reaction kinetics and avoid toxic intermediates such as H$_2$O$_2$[1–3]. On the other hand, as a gaseous electrode, large three-phase boundary areas must be established to make a close contact of oxygen with aqueous electrolytes and solid electrocatalysts, thus enabling ORR to proceed favorably[1,2]. Another kinetic obstacle for PEMFC operation is the accumulation of water as the ORR product in the cathode, which can partially obstruct or even completely interrupt the oxygen flow[4].

Nonprecious metal catalysts and their alloys are extensively investigated in the past decade with the aim to reduce material cost[5–7]. However, the ORR activity of these catalysts is mostly sluggish with an exchange current density of only 10^{-7} to 10^{-4} mA/cm^2, which is much inferior to the Pt-based catalysts[8] and is also much lower than the kinetics of conventional batteries. Although high-temperature PEMFCs could considerably enhance ORR kinetics and simplify water management[9], the development of related materials with high performance and strong durability at the high-temperature PEM environment is still a great challenge[5].

In this paper, we propose a new strategy to use a photoregenerative I$^-$/I$_3^-$ solution as an alternative cathode for PEM fuel cell, where I$_3^-$ ions participate in a discharge reaction at the cathode. Simultaneously, their reduction product I$^-$ is pumped into an external tank, where the I$^-$ ions are photoregenerated back to I$_3^-$ ions. Thus, the PEM fuel cell cathode continuously converts photoenergy into electricity through an I$^-$/I$_3^-$-mediated redox reaction.

Results and discussion

Figure 1 shows the working principle of the PEM fuel cell of this type. In this cell, the anode uses H$_2$ gas as the fuel as in conventional PEM fuel cells and delivers electrons to the external circuit by continuous oxidation of H$_2$ into protons that diffuse through the PEM into the cathode compartment for charge counterbalance. Meanwhile, the cathode-active I$_3^-$ solution is added to the cathode chamber, where the I$_3^-$ ions are electrochemically reduced to their discharge products, I$^-$ions. The I$^-$ ions are pumped into an external tank for photoregeneration. The selection of the I$_3^-$/I$^-$ couple as the cathode-active material is mainly based on the facile reduction kinetics of I$_3^-$ ions and the strong regenerative ability of I$^-$ ions to I$_3^-$ ions by photocatalysis reaction. Because the I$_3^-$ electroreduction has an exchange current density of 3.6–25 Am/cm^2 [10], which is 5–7 orders of magnitude higher than that of oxygen reduction, the I$_3^-$/I$^-$-mediated cathode offers a great benefit for PEM fuel cell applications because of the possibility to use inexpensive, nonprecious metal catalysts. Moreover, the liquid cathode can greatly simplify the structure and management of the PEM fuel cell, significantly reducing the material and operation costs.
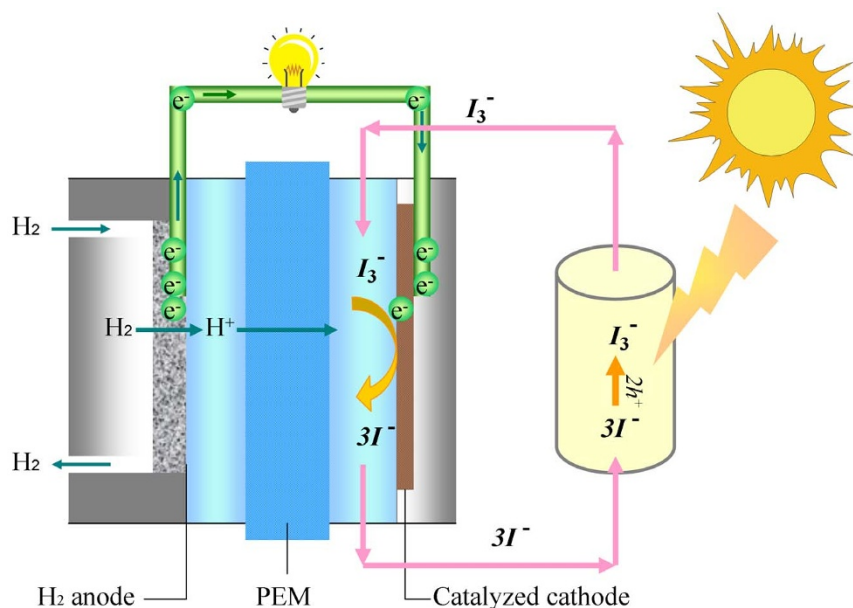
**Figure 1 | A schematic of the working mechanism of the I⁻/I₃⁻ - mediated fuel cell.**

To evaluate the discharge performance of the I^-/I_3^- redox couple as a feasible liquid cathode, we assembled a single H_2–I^-/I_3^- cell using a 2.5×10^{-3} M I_2 + 0.15 M KI + 0.5 M H_2SO_4 aqueous solution as the cathode-active electrolyte. The anode was fuelled with moist H_2 gas, and the cathode-active electrolyte was injected into the cathode chamber at 3 rpm using a peristaltic pump. The anode and cathode catalysts were made from commercially available Pt/C (Johnson Matthey) and Vulcan XC-72 carbon black (Cabot Co.), respectively. Figure 2 shows the discharge performances of the H_2–I^-/I_3^- cells measured at 5 and 65°C, respectively. As shown in Figure 2a, the cell exhibits an open circuit voltage (OCV) of 0.52 V at 5°C, which is consistent with the equilibrium redox potential (0.536 V vs. SHE[11]) of the reaction $I_3^- + 2e \leftrightarrow 3I^-$. At the discharge rates of ≤ 10 mA/cm², the cells showed a very stable discharge voltage plateau ~ 0.5 V, demonstrating only a slight cathodic polarization. When the current rate was increased, the working voltage of the cell continuously decreased similar to all conventional fuel cells. The peak power density of the cell was 12.1 mW/cm², corresponding to a cell voltage of 0.29 V. Figure 2b shows the performance curves of the cell at an elevated temperature of 65°C. At this temperature, the OCV value of the cell slightly decreased to 0.498 V, because of the negative temperature coefficient of the redox reaction of I^-/I_3^- couple. The peak power density of the cell at 65°C was greatly improved by up to 21.8 mW/cm² as compared to those observed at 5°C, corresponding to a working voltage of 0.3 V, simply due to the kinetic acceleration of the cathode reaction.

In principle, the electroreduction of I_3^- ions is a kinetically fast reaction with a very high exchange current density of 25 mA/cm²[10], as evidenced by the close similarity between the equilibrium redox potential and the observed OCV value for the I^-/I_3^- couple. However, the rate capability shown in Figure 2 seems not as high as expected. The main cause for this discrepancy is the low concentration and insufficient electrocatalysis of the I^-/I_3^- couple in this proof-of-concept experiment. Undoubtedly, further development of a highly catalytic electrode with optimized mass transport would greatly improve the discharge performance of the I^-/I_3^- cathode.

The most difficult challenge for the realization of the I^-/I_3^--mediated fuel cell is to find a simple and effective way to convert I^- ions back to I_3^- ions without consumption of fuels and electrical energy. Fortunately, the photocatalytic oxidation of I^- ions is well demonstrated to afford I_3^- ions (I_2) in aqueous solutions.

Recently[12–14], it has been reported that the photocatalyzed oxidation of I^- ions can proceed quite rapidly on a large number of metal oxides in the presence of oxygen. Considering these results, we selected TiO_2 nanoparticles as an inexpensive, nontoxic, highly stable, and efficient photocatalyst to regenerate I_3^- ions from the discharged I^- electrolyte.

Figure 3 compares the photocatalytic activities of P25 type and anatase TiO_2 nanoparticles for the photooxidation of I^- ion in H_2SO_4 solution in air. As shown in Figure 3, there is still a slow conversion of I^- to I_3^- under the irradiation of UV light, even without the existence of the photocatalyst, because of the direct chemical oxidation of I^- ions by oxygen in air. Nevertheless, the conversion rate of I^- ions was significantly enhanced from 0.07 mM without photocatalyst to 0.37 and 0.7 mM in the presence of P25 TiO_2 and anatase TiO_2 nanoparticles, respectively, after 10 min of UV irradiation. In comparison, anatase TiO_2 shows much better catalytic activity than P25 TiO_2, indicating that the crystal structure and surface geometry play an important role for the photooxidation of I^- ions. This phenomenon has also been observed in the photooxidation of I^- ions in organic media, where the higher photocatalytic activity of anatase TiO_2 than P25 TiO_2 and other oxides is attributed to the stronger suppression of the recombination of the photogenerated electron–hole pairs in these semiconductors[15]. In general, the photocatalytic oxidation of I^- ions can be expressed as follows:

$$3I^- + 2H^+ + \frac{1}{2}O_2 \xrightarrow{TiO_2(h^+)} I_3^- + H_2O \qquad (1)$$
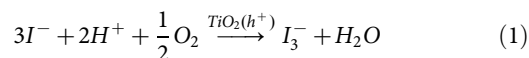
Further, the discharge reaction in the fuel cell can be expressed as follows:

$$H_2 + I_3^- \rightarrow 3I^- + 2H^+ \qquad (2)$$
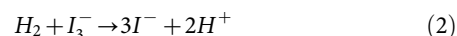
By combining the fuel cell reaction (1) with the photoregeneration reaction (2), the net reaction of this fuel cell–photoregeneration system becomes:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \qquad (3)$$

Thus, this new fuel cell actually works as a H_2–O_2 fuel cell with the I^-/I_3^- couple as the redox mediator to mediate the oxygen reduction by photocatalysis. Because the photocatalyst are mostly inexpensive metal oxides with diverse choices, it is possible to develop a highly
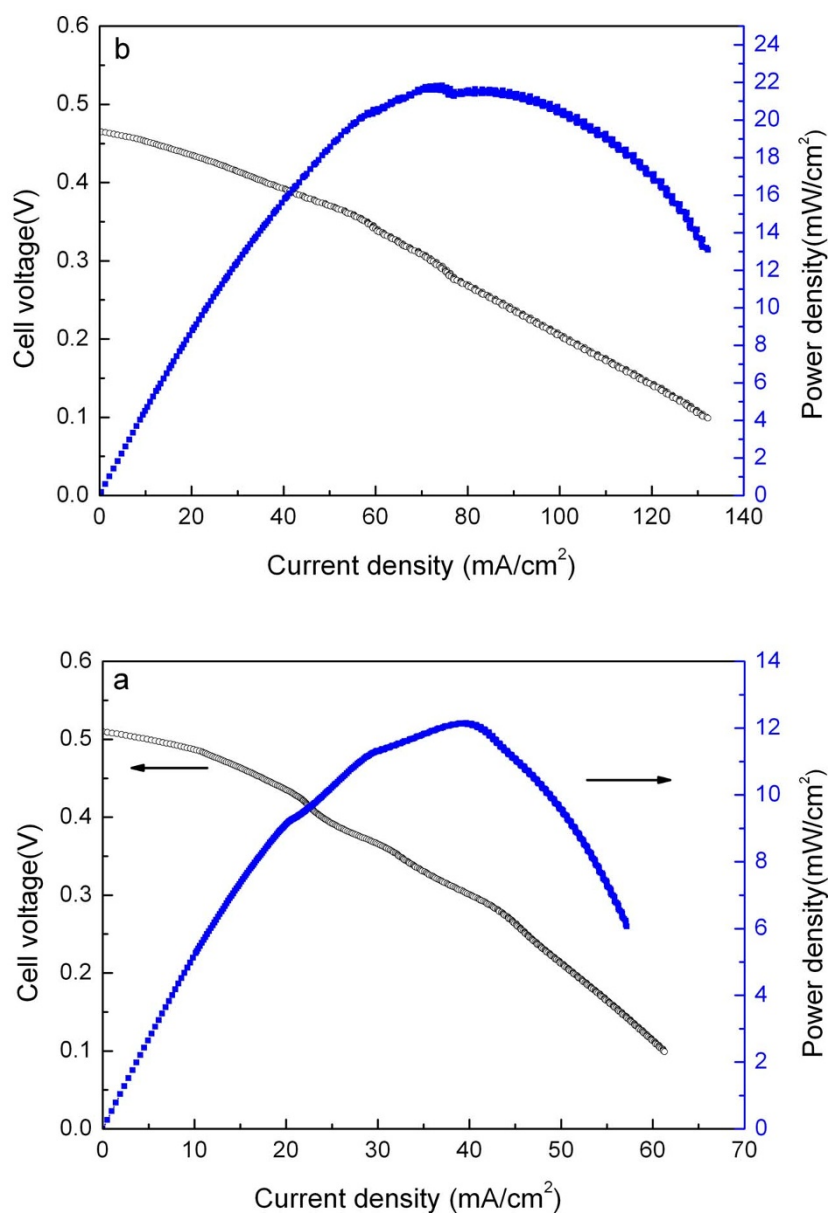
Figure 2 | Performance curves of I⁻/I₃⁻ -mediated fuel cell at different operational temperature. a. 5°C; b.65°C.

efficient photocatalytic oxidation of I^- ions to replace the direct electrooxidation of oxygen, thus the material cost for fuel cell applications.

In summary, we demonstrated an I^-/I_3^--mediated PEM fuel cell, where the direct ORR process was replaced by a kinetically favored electroreduction of I_3^- ions that are regenerated by photocatalytic regeneration of the discharged product I^- with the participation of oxygen. Such a strategy avoids the need for precious metal catalysts for sluggish oxygen reduction kinetics and also simplifies the structural design and operational management of PEM fuel cells, offering a new avenue for the development of inexpensive and environment-benign fuel cells.

Methods

Preparation of membrane electrode assemblies (MEAs) and single-cell tests: Commercial Pt/C (40 wt% Pt/C, Johnson Matthey) was used as the anode catalyst. The catalyst slurry was prepared as follows: First, 1 g Pt/C catalyst was mixed with 13 mL deionized water under vigorous stirring. Then, 6.7 mL Nafion solution (DE 520, 5 wt%, EW 1000, DuPont) was added to the mixture and ultrasonicated for 30 min, followed by high-speed homogenization for 1 h to form the catalyst slurry. Vulcan XC-72 carbon black (Cabot Co.) was used as the cathode catalyst. The pre-
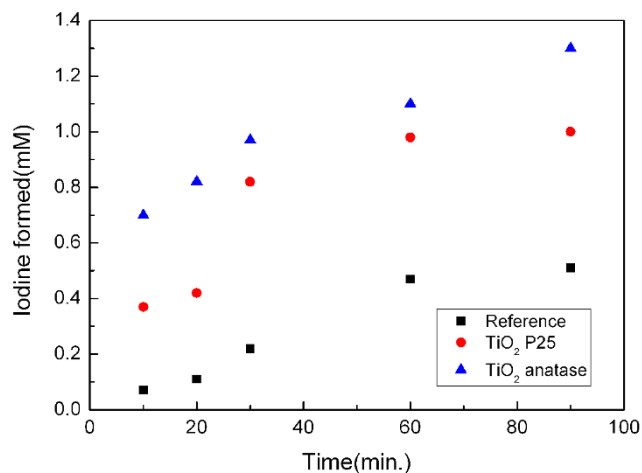

Figure 3 | A comparison of the generation rates of I_3^- in aqueous H_2SO_4 solution with addition of 0.2g P25 TiO_2, anatase TiO_2 and no catalyst (Reference).

paration of the cathode slurry is the same as that of the anode catalyst slurry except that the catalyst was changed.

The catalyst-coated membrane (CCM) method was used to prepare MEA. The catalyst slurry was applied to a PTFE thin film by spraying. After drying at 60°C for 10 min followed by the treatment at 90°C in N_2 atmosphere for 3 min, the catalyst layer was transferred onto the membrane at 125°C and 10 MPa by the decal method to form a CCM. The gas diffusion layer (GDL) was placed on the anode and cathode sides of the CCM to form an MEA.

Single cells were assembled with the prepared MEAs and graphite flow-field plates. The active area of the cell was 5×5 cm^2. H_2 was passed into the cell without humidification. Tests were carried out at specified temperatures with zero back pressure. The performance of the single cell was evaluated by measuring the polarization curve using a CHI 600A electrochemical analyzer (Shanghai CH Instruments, China).

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Acknowledgments

Author contributions

Y.W., X.A., W.M. and M.P. mconceived the project. Y.W., X.A. and Z.L. designed the experiments. Z.L. carried out the measurements. Y.W. and Z.L. analyzed the data and wrote the manuscript. All authors reviewed the manuscript.

Additional information