



Indirect fuel cell based on a redox-flow battery with a new design to avoid crossover



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HIGHLIGHTS

- A new structure for a redox flow battery to avoid crossover is proposed.
- An indirect fuel cell using the newly proposed redox flow battery was also proposed.
- The negative and positive halves of an indirect fuel cell were demonstrated separately.

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ABSTRACT

A new design of a redox flow battery (RFB), which is composed of two subcells separated by a gas phase of hydrogen, is proposed to eliminate the crossover of ionic species between the anolyte and catholyte. This idea not only increases the possible combinations of the two electrolytes, but also opens up the prospect of a revival of the old idea of an indirect fuel cell, which is composed of an RFB and two chemical reactors to regenerate the electrolytes using a fuel and oxygen. This paper describes the operation of a subcell as a component of an indirect fuel cell system. In the cycling test, oxidation/reduction of the electroactive species in each electrolyte were repeated with a hydrogen electrode as the counter electrode. This result demonstrates the possibility of this newly proposed RFB without crossover. In the operation of the subcell with a chemical reactor, a molecular catalyst (a rhodium porphyrin) was dissolved in the anolyte, and then a fuel was bubbled in the anolyte reservoir. As the electroactive species was reduced by the fuel, a steady-state oxidation current was observed at the cell. This demonstrates the negative half of the newly proposed indirect fuel cell.

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1. Introduction

A redox flow battery (RFB) is a secondary battery system composed of two tanks of two electrolytes, i.e., the anolyte and catholyte, each of which contains a soluble redox couple, and an electrochemical cell to generate electricity using the two electrolytes, which consists of two porous electrodes separated by an ion-exchange membrane [1,2]. Since this system has a unique characteristic that the magnitudes of the power and energy can be designed independently, it has been proposed as a major candidate for large-scale electricity storage systems. Based on RFB technology, the construction of an indirect fuel cell system in combination with two chemical reactors to regenerate the discharged anolyte and

catholyte using a fuel and oxygen, respectively, has been proposed for several decades, as a “chemically regenerative redox fuel cell” or “redox fuel cell” [3–5]. The concept is schematically illustrated in Fig. 1. In the anolyte regenerator, the redox couple in the anolyte is reduced by the fuel with the help of a catalyst. In the catholyte regenerator, the redox couple in the catholyte is oxidized by oxygen with the help of another catalyst. The redox flow battery is operated using these two regenerated electrolytes. Overall, electric power is obtained from the fuel and oxygen. In this system, each redox couple in the anolyte and catholyte acts as a redox mediator which mediates electron transfer from the fuel to the anode, and from the cathode to oxygen, respectively. A “partly indirect fuel cell”, which uses a mediator for only the oxygen side [6] as an improved version of a proton-exchange membrane fuel cell (PEMFC), has also been proposed.

However, except the above-mentioned partly indirect fuel cell, there is a problem to be solved before an RFB can be used to

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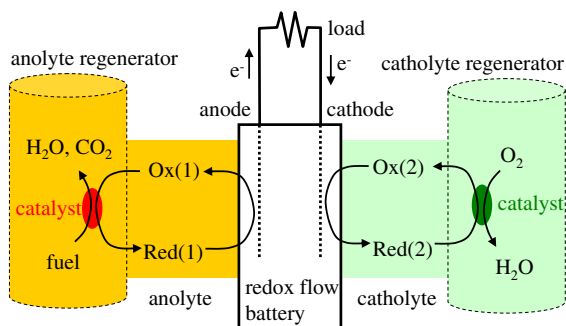


Fig. 1. Schematic of an indirect fuel cell.

construct an indirect fuel cell system. The anolyte and catholyte in an RFB are gradually mixed by diffusion through the electrolyte membrane [7]. Among the several types of RFBs that have been proposed and studied as energy storage systems [1,2], some are based on the concept of using a single element for both redox couples in the anolyte and catholyte, such as all-vanadium [8], all-chromium [9], and all-uranium [10]. This concept is an effective solution to the crossover problem, since mixing of the two electrolytes does not affect the components of the two electrolytes. Unfortunately, however, none of these RFBs can be used as a component of an indirect fuel cell system, because of the mismatch of the redox potentials. In an indirect fuel cell system, the potential of the redox mediator in the catholyte should be slightly lower than the open-circuit potential (OCP) of the oxygen electrode (ca. 1 V), while that in the anolyte should be slightly higher than the OCP of the hydrogen electrode (0 V). All-vanadium (or any other single element type) system does not satisfy this demand, and at this stage we have to use two different elements for redox mediators. This raises the crossover problem of mixing of two redox mediators, which represents irreversible deterioration of the system.

To help realize the commercial application of an indirect fuel cell, here we propose an RFB with a new design to avoid the crossover problem. Fig. 2 shows its concept in comparison with a conventional system. The new design incorporates negative and positive subcells connected in series. During a discharge process, the negative subcell combines oxidation of the anolyte at a porous electrode as an anode and the hydrogen evolution reaction (HER) at a gas diffusion electrode (GDE) as a cathode, whereas the positive subcell combines the hydrogen oxidation reaction (HOR) at a GDE as an anode and reduction of the catholyte at a porous electrode as a cathode. Since the anolyte and catholyte are separated by a gas phase of hydrogen, any species in the electrolytes, except water vapor, are blocked. As noted in Fig. 2(b), the cathode of the negative subcell, the anode of the positive subcell, the electric wire connecting them, and the gas phase of hydrogen act together as a proton-permeable membrane.

The two subcells in Fig. 2(b) have a common structure: a porous electrode for an electrolyte and a GDE for hydrogen. A half-cell can be tested independently with any electrolyte, regardless of whether it is intended to be used as an anolyte or catholyte in this system. This means that experiments to develop our new RFB are easier than those for a conventional RFB, in which reactions of the anolyte and catholyte can not be performed separately, and matching of the state-of-charge (SOC) of the two electrolytes should always be considered when interpreting the results. After we determine the performance of various electrolytes against hydrogen, we can estimate the performance of a hypothetical system constructed with a choice of any two electrolytes as the anolyte and catholyte.

The objective of this work was to examine the feasibility of two technologies which are essential for realizing our proposal of an indirect fuel cell system: the operation of a subcell of the new RFB,

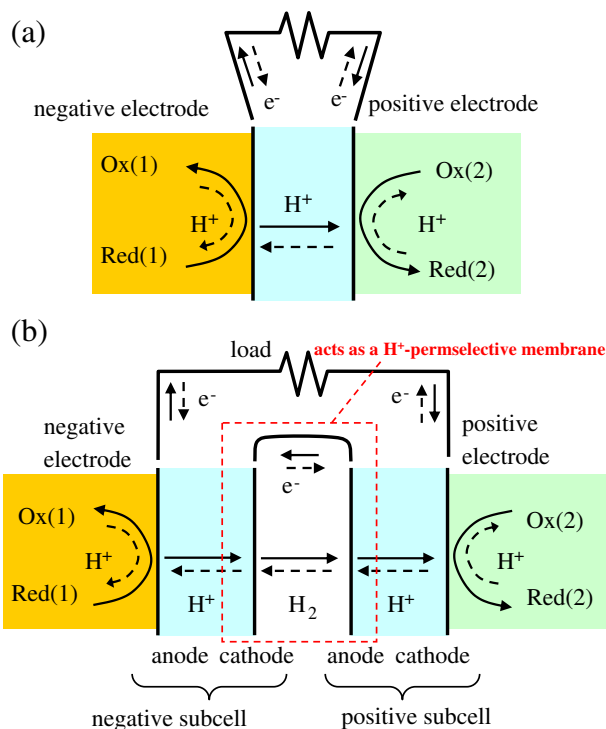


Fig. 2. Schematics of (a) conventional and (b) newly proposed RFBs. Dotted arrows represent inverse (charging) directions.

and the operation of a chemical reactor to regenerate the electrolyte. In the operation of a subcell, iron, indigocarmine, and an anthraquinone derivative were tested as electroactive species in the electrolytes. For each electrolyte, reduction/oxidation cycles of the electrolyte were performed against a hydrogen electrode. In the operation of a chemical reactor, an electrolyte containing an oxidized species was chemically reduced by carbon monoxide or hydrogen, with the aid of a rhodium porphyrin as a molecular catalyst. The steady-state operation of a subcell in combination with a chemical reactor was also tested.

2. Experimental

2.1. Subcell

A schematic illustration of the fabricated subcell is shown in Fig. 3. This represents a combination of PEMFC technology on the left half and RFB technology on the right half. The geometric active area of the electrodes was 2.25 cm². For the left side of the subcell, a unitized block with a casing and a flow field of H₂ was made of

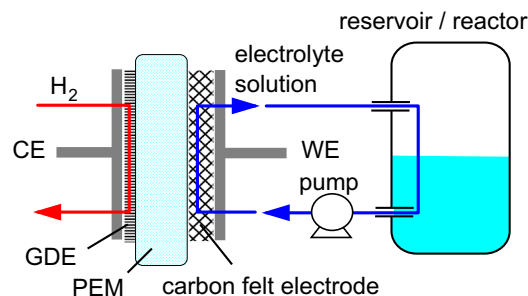


Fig. 3. Subcell consists of a gas diffusion electrode for hydrogen and a porous electrode for an electrolyte.

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