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Review

Process engineering in electrochemical energy devices innovation☆

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ABSTRACT

This review focuses on the application of process engineering in electrochemical energy conversion and storage devices innovation. For polymer electrolyte based devices, it highlights that a strategic simple switch from proton exchange membranes (PEMs) to hydroxide exchange membranes (HEMs) may lead to a new-generation of affordable electrochemical energy devices including fuel cells, electrolyzers, and solar hydrogen generators. For lithium-ion batteries, a series of advancements in design and chemistry are required for electric vehicle and energy storage applications. Manufacturing process development and optimization of the $LiFePO_4$/C cathode materials and several emerging novel anode materials are also discussed using the authors' work as examples. Design and manufacturing process of lithium-ion battery electrodes are introduced in detail, and modeling and optimization of large-scale lithium-ion batteries are also presented. Electrochemical energy materials and device innovations can be further prompted by better understanding of the fundamental transport phenomena involved in unit operations.

1. Introduction

To address the growing challenges from depleting fossil fuel reserves, increasing world population, growing expectations for high living standards, and rising concerns over air quality and climate change, one possible solution is to develop an alternative energy system that is safe, clean, and sustainable, in place of the current major energy system that is based on the combustion of fossil fuels. Combustion has played a leading role in energy conversion throughout human history. In a combustion process, reduction and oxidation (redox) reactions are coupled together, and electrons are transferred directly from the fuel to the oxidant to produce heat. By contrast, in an electrochemical process, the redox reactions are spatially separated by an electrolyte, allowing electrons to do work as electricity which leads to intrinsically higher energy conversion efficiency yet in relatively milder conditions, compared with combustion process. Electrochemical energy engineering can be regarded as a sub-discipline of chemical engineering, and it is also closely related to process engineering.

Electrochemical energy engineering research fields typically include: (1) electrocatalysis and electrode reaction kinetics; (2) electrolyte materials and ion transport; (3) device design and the corresponding electrode materials and manufacturing; (4) electrochemical energy system engineering; and (5) electrochemical energy device evaluation technologies. As a way to timely highlight the research work in the innovation for the process engineering in electrochemical energy devices, an integrated electrochemical energy system is envisioned that consists of the following electrochemical energy devices: energy storage (ES), fuel cells (FCs), electrolyzers (ELs), and solar hydrogen generators (SHs) (Fig. 1).

Solar panels and wind turbines can provide clean and renewable electricity and they are integrated into electric grid which is equipped with electrochemical energy storage devices, such as lithium-ion batteries and redox flow batteries. Fuel cells coupled with solar hydrogen generators and/or water electrolyzers can provide clean power for transportation and buildings. With minor variations, all the aforementioned electrochemical devices have the same basic three-layer structure (electrode/membrane/electrode) [1].

This article provides a perspective, rather than a comprehensive review. Hence, we use mostly our own recent work as examples to show the strategic switch of polymer electrolytes from PEMs to HEMs for fuel cells, and to demonstrate the innovative electrode designs and manufacturing for lithium-ion batteries.

2. From PEM Fuel Cell to HEM Fuel Cell

2.1. Key features of HEM fuel cells

Fuel cells are electrochemical devices which convert chemical energy stored in fuels to electricity. Fuel cells are intrinsically superior to combustion for chemical-to-electrical energy conversion in terms of conversion efficiency and environmental friendliness. Owing to the separation between the two electrodes, fuel oxidation, oxidant reduction, ion conduction through the electrolyte, and electric load can be

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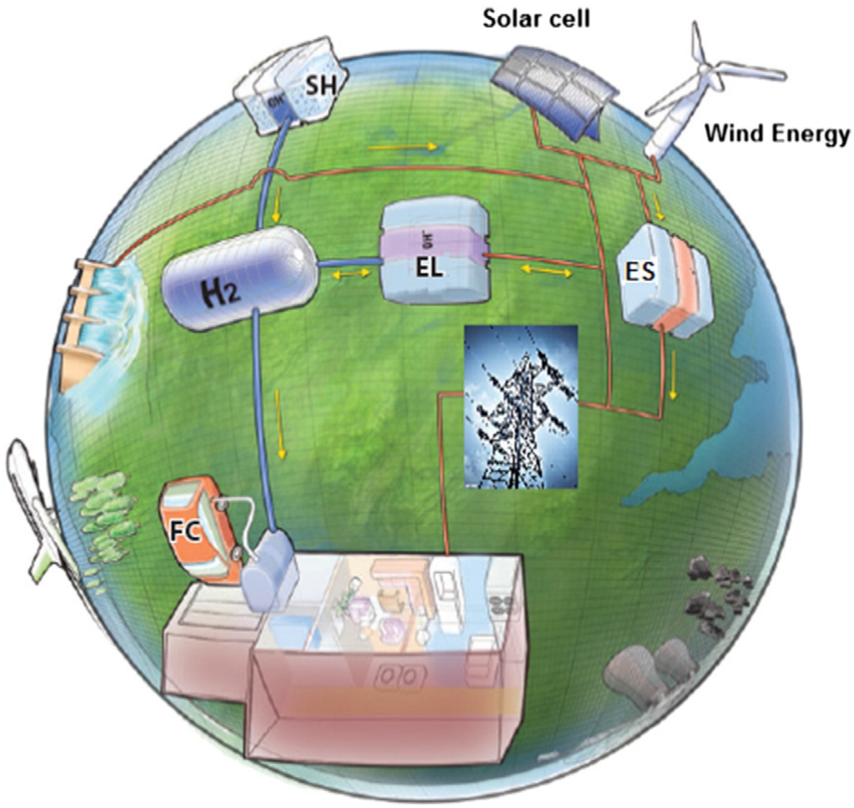

Fig. 1. An integrated, safe, clean, and sustainable electrochemical energy system based on fuel cells (FCs), solar hydrogen generators (SHs), electrolyzers (ELs), and energy storage (ES). With minor variations, all the aforementioned electrochemical devices share the same basic three-layer structure: electrode/membrane/electrode.
Adapted from the Ref. [1].

engineered individually, and such independent engineering of each component creates excellent flexibility in device design and diagnosis. Fuel cells have been considered as promising power sources for stationary and vehicular applications. In particular, hydrogen-fueled low-temperature (typically below 100 °C) fuel cells are very attractive because hydrogen has high specific energy (34 $kW\cdot h\cdot kg^{-1}$, or 2.6 times that of gasoline), and the use of hydrogen can be free of carbon footprints if hydrogen is obtained from solar water splitting or other renewable methods.

Usually, the nature of the electrolyte used in the fuel cell dictates the selection of its electrode materials and the operational conditions. Therefore, the fuel cells are generally categorized by their electrolytes utilized.

In 1950, solid polymer electrolytes, *i.e.*, PEMs (based on a sulfonated polystyrene polymer), were invented [2]. Similar to liquid acids, solid PEMs are also conductive for protons but are much more convenient and safer to handle for fuel cell applications. PEMs are completely free of electrolyte leakage problems. For these reasons, PEMs were quickly adopted as a new category of electrolytes into fuel cells (*i.e.*, PEM fuel cells, or PEMFCs) replacing the liquid acids in 1955 [3].

Nafion's ability to serve as both membrane and ionomer and its outstanding chemical, thermal, and mechanical stability have enabled PEMFCs to achieve high specific power (above 1 $kW\cdot kg^{-1}$) and good device durability (over thousands of hours) [4]. The success of PEMFCs has stimulated the research and commercialization interests in fuel cells over the past half-century.

PEMs provide a proton-mediated environment for electrode reactions in PEMFCs and thus precious metals (typically Pt) are demanded as electrocatalysts for PEMFCs. Largely due to their thermodynamic instability in proton-mediated environments, stable yet active nonprecious metal-based electrocatalysts have been very challenging to develop for PEMFCs [5–7].

Nonprecious metals have much better stability in base than in acid, and they are also more active in base. For example, Ni and Ag were successfully demonstrated as active and chemically stable nonprecious HOR and ORR electrocatalysts, respectively, in strongly alkaline solutions [8]. The idea of introducing HEMs, the counterpart of PEMs, to fuel cells can be traced back as early as PEMFCs. In part due to the great success of PEMFCs, not much work has been carried out in developing HEM fuel cells (HEMFCs). To eliminate the heavy dependence on precious metals of PEMFCs, the concept of HEMFCs was brought back to the fuel cell research community in 2001 [9,10]. The working principle of HEMFCs is shown in Fig. 2, and electrode reactions are as follows (based on pH = 14; SHE, standard hydrogen electrode):

$$\text{Anode reaction(HOR)}: 2H_2 + 4OH^- \rightarrow 4H_2O + 4e^- \quad (1)$$
$$E^o = -0.828\,V \textit{ versus } SHE.$$

And the complete (four-electron) O_2 reduction in alkaline environment is:

$$\text{Cathode reaction(ORR)}: O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (2)$$
$$E^o = 0.401\,V \textit{ versus } SHE.$$

As polymer electrolytes, HEMs are convenient and safe to handle, similar to PEMs. The advantage of HEMFCs over PEMFCs is their ability to work with nonprecious metal-based electrocatalysts, enabled by the hydroxide-mediated environment in HEMs.

2.2. Key components of HEMFCs

2.2.1. HEMs and HEIs

An HEM is placed between the anode and the cathode, and it plays three major roles: a) an ionic conductor offering hydroxide transport between the two electrodes to continue their electrochemical reactions;