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Mini Review

A Review of Recent Research Progress and Prospects of Direct Borohydride Fuel Cells (DBFC)

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Abstract

As global energy demand increases dramatically, the fossil energy system dominated by coal, oil, and natural gas has limited its wider application due to its high pollution and high carbon emission drawbacks. Alternative and clean new energy systems are being developed worldwide. DBFCs, as an outstanding class of PEMFCs, are gaining more and more enthusiasm from scholars for their potential in energy applications.

Keywords: DBFC; PEMFC; NaBH4; Electrochemical oxidation; Fuel cell

Abbreviations: Direct borohydride fuel cells (DBFC); Proton exchange membrane fuel cell (PEMFC); Direct methanol fuel cells (DMFC); Sodium borohydride (NaBH4); Cation-exchange ionomer (CEI); Anion-exchange ionomer (AEI); pH-gradient-enabled microscale bipolar interface (PMBI)

Introduction

At present, with the worldwide rapid economic development, the reliance on traditional fossil energy sources such as coal, oil and natural gas is gradually increasing, however, the burning of large amounts of fossil energy has caused great damage to the human living environment, such as the frequent occurrence of hazy weather and the greenhouse effect in recent years. All these remind us to reform and improve the current energy structure, so it is the common expectation of people all over the world to explore and develop a high efficiency and high-capacity clean energy.

In 1839, the British scientist William Robert Grove introduced the concept of fuel cell by reversing the electrolysis of water and discovering that an electric current was generated [1]. The fuel cell (FC) is capable of converting chemical energy from conventional fuels into electrical energy directly without going through the process of combustion. Due to its high conversion efficiency (up to 80%) and zero emission (the product is mainly H_2O), it is widely used in cell phones, portable computers, new energy vehicles, and other fields, and is a promising class of clean energy.

Due to a series of advantages such as fast start-up, high power density, and easy operation, PEMFCs have evolved rapidly and become more and more popular in recent years. However, PEMFC using H_2 as fuel is still far from industrialization because of the difficulty of storage and transportation, safety of the fuel used, and the high price of Pt metal used as anode. For this reason, attention has been turned to the research of fuel cells fueled by liquid hydrogen-containing compounds, among which direct methanol fuel cells

(DMFC) have been favored. This kind of fuel cell is a kind of PEMFC using methanol as fuel, which has a series of advantages such as high hydrogen content, wide fuel source and low price, and is a very promising fuel cell. These have seriously hindered the commercialization of DMFC [2]. As another new fuel cell, the emergence of DBFC has attracted more and more attention from researchers.

DBFC is one of the low-temperature PEMFCs, which uses a fuel of $NaBH_4$ (or KBH_4) solution under alkaline conditions, and the cathode oxidizer can be air (Air), oxygen (O_2), or hydrogen peroxide (H_2O_2). DBFC has many advantages over other liquid fuel cells, such as top theoretical open circuit potential (1.64 V), Outstanding energy density (9300 Wh kg^{-1}), and clean products [3]. However, during the operation of DBFC, water-resolved hydrogen occurs due to BH_4^-, which not only reduces the fuel utilization but also poses a safety hazard. And then, the current expensive anode materials severely limit the industrialization of DBFC. As such, the development of anode materials with both cheap and high catalytic activity that can effectively promote the oxidation of BH_4^- and inhibit the hydrolysis of BH_4^- will be an important direction for future researchers to work on.

Overview of DBFCs

$NaBH_4$, also known as sodium tetrahydroborate, sodium hydroborate, molecular weight 37.83, is a solid white powder, non-toxic, non-combustible, stable at room temperature, soluble in water, liquid ammonia, polyether, and easily absorbs water in air to generate $NaBH_4{\cdot}2H_2O$. Because of its strong reducing properties, $NaBH_4$ is often used in a wide range of organic and inorganic reactions. In the last few decades, $NaBH_4$ has been found to be applied in electrochemical energy conversion, as a hydrogen storage substance and as a fuel for power generation in fuel cells [4]. Compared with other types of PEMFCs, DBFC has the following advantages:

- $NaBH_4$ as a solid fuel is easier to store and transport, and $NaBH_4$ is safe and non-toxic, chemically stable, and has a high hydrogen content of 10.6 wt.% [5].
- DBFC products are H_2O and sodium metaborate ($NaBO_2$), which are environmentally friendly and pollution-free, and $NaBO_2$ can be recycled and converted to $NaBH_4$ under certain conditions [6].
- DBFCs have superior theoretical voltage and outstanding theoretical energy density. The theoretical energy density of DBFC is 9.3 Wh g^{-1}, while that of DMFC is only 6.1 Wh g^{-1}[7].

Based on a series of advantages of DBFC, people have never stopped paying attention to it and exploring it. The DBFC was first reported and discovered by Amendola et al., [8], who experimentally derived a maximum power density of 60 mW cm^{-2} for the cell at 70 °C in air. Since then, a large number of articles on DBFC have been published. It is exciting that DBFC has superior application potentials in new energy electric vehicles, deep space exploration and deep-sea exploration.

DBFC is currently favored by many researchers due to its high theoretical energy density and clean products, but there are still many critical issues to be solved to achieve commercialization [9]. For example, (1) $NaBH_4$ will undergo varying degrees of hydrolysis during oxidation, which will lead to lower fuel utilization, and the H_2 produced by hydrolysis will pose a safety hazard [10]. (2) During DBFC operation, $NaBH_4$ permeates between the electrodes, generating a mixed potential and intensifying electrode polarization. (3) Currently, the anode catalysts used for DBFC are a series of precious metals such as Au, Pt, Ag, Pd, etc., which undoubtedly increases the cost of DBFC. For this reason, related researchers at home and abroad have mainly focused on anode catalysts, electrolyte diaphragms and cathode catalysts, among which, the most intensively studied are the preparation of various anode catalytic materials and the electro-oxidation behavior of $NaBH_4$ on various anode catalytic materials.

Recently, a novel and innovative PMBI configuration of DBFC (power density: 630 mW cm^{-2}) was prepared by Zhongyang Wang et al., [1]. The PMBI configuration can maintain a high open-circuit voltage (1.94V) at which water electrolysis is not easily occurring, thus increasing the efficiency of the DBFC. In addition, the effect of CEI and AEI in Ni-based materials on DBFC performance (power density: 590 mW cm^{-2}) was investigated in depth by Youngdon Ko et al., [11]. The results demonstrate that CEI-Ni can effectively adsorb BH_4^- intermediate species in the fuel cycle and has high tolerance to BH_2^-. At once, a carbon film-coated non-precious metal NiMoN@NC [12] catalyst was employed for energetic DBFC (power density: 67 mW cm^{-2}). DFT calculations showed that Ni is the active site and the rate determining step of the reaction is $^*B(OH)_2 \rightarrow {}^*B(OH)_3$. Meanwhile, theoretical calculations have proved that the PdNi alloy has weaker -H and -OH adsorption than Pd and Ni alone and can better adsorb BH_4^- intermediate species in the reaction. The PdNi/C [13] material synthesized based on this theory obtained outstanding DBFC performance (power density: 630 mW cm^{-2}). It was demonstrated that doping Zn into the Ni shell as the core to form Ni@Zn [14] with high index surface can optimize the $NaBH_4$ electro-oxidation ability of Ni and boost the DBFC properties (power density: 180.3 mW cm^{-2}).

Prospects

DBFC is a fuel cell system with great potential, compared to other energy-containing hydrogen storage fuel cell systems. However, there are still obvious drawbacks that limit the expansion of its application. High Pt-containing electrode materials are among the main factors limiting its diffusion, and the development of catalytic electrode materials that can replace Pt is a hot spot for researchers to focus on in the future. There are two ways to solve this problem, one is to improve the atomic utilization rate and anti-toxicity ability of Pt catalysts to reduce the cost of materials used; the other is to find alternative Pt, such as Ni-based and cobalt-based materials, to eliminate the use of Pt fundamentally. These two directions are currently the focus of scholars' research in catalysts.

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Conflict of Interest

No conflict of interest.

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