

Direct Liquid Fuel Cells: A Research Progress and the State of the Art

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ABSTRACT

Direct liquid fuel cells offer many advantages of that directly converts chemical energy into electric energy for power generation with easily obtaining fuels without fuel reforming including wastes or pollutants and such oxidants like heavy metals under common conditions. This work summarizes recent advances and progress mainly on the catalysis studies and their mechanism as well as some typical examples of fuel cell's assemblies or redox pairs. The pioneering works of our laboratory indicated the technology is not only feasible but also applicable. Further investigations are required including fuel cell's output current density and applicability.

Keywords: direct liquid fuel cells, oxidants, catalysts

1. DIRECT LIQUID FUEL CELLS

Fuel cell is a device that converts chemical energy into electricity. It converts chemical energy stored in fuels and oxidants into electrical energy under isothermal condition according to electrochemical principle. In the 1990s, the proton exchange membrane fuel cell (PEMFC) has made a breakthrough by using hydrogen as fuel. However, hydrogen is difficult to store and transport, which hinders the commercialization of PEMFC. Thus, scientists began to look for alternative fuels. Due to the high energy density, low molecular weight organic compounds have been widely receiving much more attentions because they are rich in hydrogen and easy transportation.

Direct liquid fuel cell (DLFC) is a kind of cell that directly supplies fuels to fuel cell without fuel reforming and converts chemical energy into electric energy for

power generation. Small molecular hydrogen rich materials have become the important choice objects of direct liquid fuel cell as fuel, mainly including methanol, ethanol, formic acid, glucose, sodium borohydride, urea, hydrazine, ammonia, etc. Among them, alcohol fuel cells have the most research and development prospects. The typical representatives are direct methanol fuel cells (DMFCs) and direct ethanol fuel cells (DEFCs). Alcohol fuel cell uses alcohol as fuel directly, and its aqueous solution is easy to carry and store. Many reports have described the principle of DMFCs and DEFCs. [1]

However, methanol is toxic and fuel penetration is serious, as well as the slow oxidation kinetics of ethanol containing C-C bond, people are also looking for other liquid fuels containing hydrogen. Therefore, direct formic acid fuel cell (DFAFC) [2], direct glucose fuel cell (DGFC) [3] and direct hydrazine fuel cell (DHFC) [4] are widely concerned and well studied. Those alternative fuels possesses many advantages of high energy density and easy to obtain. For formic acid, it is a non-toxic food additive, with high energy density and high electromotive force, and its passing through lower than methanol (partially dissociated into methylate ion in solution). Glucose can produce high energy and is easy obtained raw material without explosion risk. Hydrazine has a hydrogen content of up to 12.5 wt%, the same as methanol and higher than NaBH₄, only nitrogen and water are its byproducts, which will not emit greenhouse gas CO₂.

The direct sodium borohydride fuel cell (DBFC) with sodium borohydride (NaBH₄) aqueous solution as fuel has special advantages: the performance of solid fuel is stable and nonflammable, the battery voltage is high

(1.64 V), the specific energy is high (5.7 Ah/g, higher than 5.03 Ah/g of methanol), so the relevant research arises [5].

Table 1. Brief summary of the oxidation reactions at anodes and total reactions with oxygen as an oxidant of liquid fuel cells

Fuel	Anodic reaction	Total reaction
Methanol	$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$	$\text{CH}_3\text{OH} + 3/2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}, E^0 = 1.21 \text{ V}$
Ethanol	$\text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^-$	$\text{C}_2\text{H}_5\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}, E^0 = 1.15 \text{ V}$
Formic acid	$\text{HCOOH} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$	$\text{HCOOH} + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{CO}_2, E^0 = 1.48 \text{ V}$
Glucose	$\text{C}_6\text{H}_{12}\text{O}_6 + 24\text{OH}^- \rightarrow 6\text{CO}_2 + 18\text{H}_2\text{O} + 24\text{e}^-$	$\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O}$
Hydrazine	$\text{N}_2\text{H}_4 + 4\text{OH}^- \rightarrow 4\text{H}_2\text{O} + \text{N}_2 + 4\text{e}^-$	$\text{N}_2\text{H}_4 + \text{O}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}, E^0 = 1.56 \text{ V}$
Sodium borohydride	$\text{BH}_4^- + 8\text{OH}^- \rightarrow \text{BO}_2^- + 6\text{H}_2\text{O} + 8\text{e}^-$	$\text{BH}_4^- + 2\text{O}_2 \rightarrow \text{BO}_2^- + 2\text{H}_2\text{O}, E^0 = 1.64 \text{ V}$

To sum up, the fuel in the fuel cell is hydrogen, liquid hydrogen or hydrogen rich organic matter (Table 1). Through the catalytic action of catalyst, these fuels are electrically oxidized to release electrons and protons, which are supplied to the cathode oxidant through the external circuit, and protons form a circuit through the membrane electrolyte. Some pollutants in wastewater are rich in hydrogen, such as urea, phenol, ethanol, formaldehyde, etc. These H-rich pollutants can also be used as fuel options.

2. CATALYTIC CONVERSION OF FUELS

2.1 Catalyst carriers for fuel cells

The oxidation of fuel in DLFC needs to take place under the action of catalyst. Catalyst is an important material in all parts of fuel cell, its activity directly affects the output performance of the whole cell. Generally, the catalyst is coated on the base material to form a catalytic anode. The matrix materials include carbon fiber cloth, carbon paper, nickel foam and so on. The catalytic reaction of fuel at the solid-liquid interface belongs to heterogeneous reaction, and the slow electrode kinetics can be solved by the catalyst adsorbed on the electrode surface. Because of its excellent catalytic properties, such as precious metals and their alloys, metal nanoparticles are widely used in fuel cells and are often chosen by researchers. High surface area can increase the reaction rate. In order to

obtain nano scale metal particles with high dispersion, high utilization efficiency and good stability, the catalyst carrier can be used. It is a common method to load metal nano catalyst onto catalyst support by certain methods.

Compared with the whole metal catalyst, the supported catalyst shows better activity and stability. In the supported metal particle catalyst, the support plays the role of dispersion and fixation of the catalyst. It is one of the places where the catalytic reaction takes place, and it is also the intermediate medium of material transfer and electronic transmission. For example, the dispersion of platinum metal particles, the interaction of multiple metals, and the interaction of catalyst and support are all related to the support. Therefore, the carrier material should have the characteristics of good conductivity, large specific surface area, reasonable pore structure, and excellent corrosion resistance, which are generally the criteria for carrier selection. The main catalyst supports include carbon black [6], carbon nanotubes [7], carbon nanofiber [8], carbon gel [9], conductive polymer [10] and new developed graphene [11]. The carbon black with low surface area can not get high dispersed catalyst particles, while the carbon black with high surface area can get high dispersed catalyst particles. Ordered carbon nanotubes have better performance than carbon black, but disordered carbon nanotubes can not make full use of the catalyst. Carbon nanofibers have the characteristics of high conductivity, low resistance and high surface area, which can be prepared by chemical vapor deposition. The carbon gel can react with phenol resin to form gels, which can be obtained by pyrolysis reaction under high temperature inert atmosphere. The characteristics are the tortuous open loop structure and high surface area. Conducting polymers have both electron and proton conducting properties. Graphene is a new carbon material developed in recent years. It has good electronic conductivity and huge specific surface area ($2630 \text{ m}^2 \text{ g}^{-1}$). It has great potential as a catalyst carrier, but its preparation cost is high and its performance is not well controlled. At present, carbon black is still the most commonly used carbon carrier.

2.2 Catalyst preparation

In recent years, the preparation of catalysts has become a very important topic in the development of fuel cell electrode catalysts. When the catalyst is supported on some porous and large surface area supports, the catalyst utilization efficiency can be

greatly improved, and the agglomeration of catalyst can also be prevented during the use of fuel cell. The preparation methods of electrocatalysts include physical method and chemical method. Physical method is to prepare nanometer sized particles from bulk metals through some treatment, such as sputtering, thermal evaporation and physical vapor deposition (PVD), and then load them onto carbon carrier. Physical method is simple to prepare, but the prepared nanoparticles are relatively large (tens to hundreds of nanometers), and it is difficult to control the size of nanoparticles [12]. Chemical synthesis of nano metal particles is the most common method of synthesizing metal nanoparticles in recent years. The three main methods include impregnation reduction, colloidal and microemulsion methods. These methods include the steps of forming nanoparticles and the steps of carrying particles onto the carrier.

The anode of DLFC usually uses platinum as catalyst. After the fuel such as methanol adsorbed on the platinum surface, the hydrogen atom was adsorbed by the multi-step dehydrogenation reaction, and the hydrogen atom further reacted with the anode to form protons and electrons, at the same time, CO and other intermediate products were generated. Due to the strong adsorption capacity of CO on Pt surface, it can occupy the active site of Pt catalyst surface, thus reducing the catalytic activity of Pt, leading to serious poisoning of Pt catalyst. For this reason, Pt based metal alloy catalysts were prepared by adding a second metal (Ru [13], Au [14], Pd [15], Rh [16], Ir [17], Bi [18], Sn [19], Ni [20], Co [21] and Fe [22]) to Pt based catalysts to alleviate poisoning. Through the preparation of various Pt based alloy catalysts, the aggregation state and existing form of the catalysts are improved, and the catalytic activity is improved.

2.3 Catalytic mechanism

Due to the limited reserves and high price of platinum, it is hoped that Pt cannot be good candidate as the electrocatalyst of DLFC. Compared with precious metals, nickel is rich in abundance, good in corrosion resistance, low in price and excellent in electrocatalysis, so it is widely used in electrocatalysis, organic synthesis and other fields. Nickel and nickel based metals have good catalytic performance for the oxidation of small organic compounds such as methanol, ethanol, urea, etc. The toxicity of Ni based electrode is less than that of Pt based electrode. The oxidation potential of most organic compounds coincides with that of nickel electrode. Ni(OH)₂/NiOOH plays a key role in the

electrochemical oxidation of organic compounds. Taraszewska and Roslonek [23] found that Ni(OH)₂ modified glassy carbon electrode played an effective role in methanol oxidation. The oxidation of urea on nickel electrode in alkaline solution shows that [24], nickel reacts with KOH to form Ni(OH)₂, and then NiOOH, which is oxidized from Ni(OH)₂, catalyzes the oxidation of urea.

In our group, we employed in-situ electrochemical and surface enhanced Raman spectroscopic (SERS) method to characterize catalytic behaviors of Ni during the electro-oxidation of urea. Ni catalyst on Au layered glassy carbon electrode showed potential dependent. SERS signal exhibits that at oxidation potential the presence of urea in alkaline medium caused the decrease in Raman intensities of NiOOH and urea to accompany with appearance of Ni(OH)₂ Raman band. It implies that NiOOH has been chemically reduced to Ni(OH)₂ by urea and given obviously an evidence that the electro-oxidation of urea is mediated through the NiOOH/Ni(OH)₂ redox pair and follows the catalyst regeneration mechanism.

3. OXIDANTS IN DIRECT LIQUID FUEL CELLS

Energy extraction can be achieved electrochemically similar to thermal combustion, both of which require fuel to provide electron and electron acceptor (oxidant). The conventional fuel cell uses oxygen or air as oxidant, as cathode electron acceptor. Under the action of catalyst, oxygen receives the electrons transferred from anode to produce reduction reaction, and generates current under external load. Hydrogen peroxide is also used as an oxidant in the development of fuel cells, such as sodium borohydride hydrogen peroxide fuel cells [25].

In addition to hydrogen peroxide, soluble chemicals can also be used as oxidants (Table 2), such as nitrate, sulfate, heavy metal ions, etc. Heavy metal wastewater contains various metal ions. It is a new idea to use catalysis technology to deal with heavy metal with self generated electricity, and there are few works reported in literature. In our laboratory, we demonstrated a strategy of reducing Cr(VI) by human urine with self-generation electricity via a urine/Cr(VI) fuel cell (UCrFC), in which urine functions as fuel and Cr(VI) serves as oxidant. Fresh urine is electro-oxidized on carbon supported nano-Ni catalyst at anode and strong acidic Cr(VI) synthetic wastewater is electro-reduced at catalyst-free cathode. An ion selective separator, consisting of an anion exchange membrane and a cation exchange membrane, is introduced to improve the cell

performance by hindering the crossover of dichromate and ammonium. Using 50 mg/L Cr(VI) in 0.25 M H₂SO₄ as catholyte, neat urine as anolyte, the maximum power density of UCrFC reached 3.4 W/m² with an open circuit voltage (OCV) of 1.3 V. More than 90% of Cr(VI) was reduced with coulombic efficiency of more than 98%, meanwhile total carbon and nitrogen in urine was also removed with efficiency about 78%. The effects of initial Cr(VI) and H₂SO₄ concentration were investigated. The specific capacity of UCrFC reached 4417 mAh per liter of human urine. [26]

Similarly, to eliminate contaminants like phenol and dichromate from aqueous solutions is still a hot topic of research interest. Instead of energy input, both dichromate and phenol were removed within self-powered process through a phenol-Cr(VI) coupled redox fuel cell reactor, which was uniquely assembled on Ni/C anode the electro-oxidation of phenol takes place to give electrons and then go through the external circuit reducing Cr(VI) to Cr(III) on the cathode. [27]

Energy-free denitrification of N-rich wastewater was explored to be feasible, in a self-powered device ammonia/nitrate coupled redox fuel cell (CRFC) reactor was served as removing nitrogen and harvesting electric energy simultaneously. Ammonia is oxidized at anodic compartment and nitrate is reduced at cathodic compartment spontaneously by electrocatalysis. In 7.14 mM ammonia + 0.2 M KOH anolyte and 4.29 mM KNO₃ + 0.1 M H₂SO₄ catholyte, the nitrate removal efficiency was 46.9% after 18 h. Meanwhile, a maximum power density of 170 mW/m² was achieved when applying Pd/C cathode. When NH₄Cl/nitrate and ammonia/nitrite CRFCs were tested, 26.2% NH₄Cl and 91.4% NO₂⁻ were removed respectively. Nitrogen removal efficiency for real leachate at the same initial NH₃ concentration is 22.9% and nitrification of ammonia in leachate can be used as nitrate source. This work demonstrated a new way for N-rich wastewater remediation with electricity generation. [28]

Energy extraction from waste has attracted much interest nowadays. Herein, a coupled redox fuel cell (CRFC) device using heavy metals, such as copper, as an electron acceptor is assembled to testify the recoveries of both electricity and the precious metal without energy consumption. The CRFC demonstrated that useful chemicals were recovered and the electricity contained in the chemicals was produced in a self-powered retrieval process. [29]

The recovery of heavy metals from aqueous solutions or e-wastes is of utmost importance. Retrieval

of Au, Ag, and Cu with electricity generation through building an ethanol-metal coupled redox fuel cells (CRFCs) is demonstrated. The cell was uniquely assembled on PdNi/C anode the electro-oxidation of ethanol takes place to give electrons and then go through the external circuit reducing metal ions to metallic on the cathode, metals are recovered. When gold and copper ions coexist, it was confirmed that metallic Cu is formed on the cathodic electrode later than metallic Au formation by XPS analysis. Thus, this system can achieve step by step electrodeposition of gold and copper while the two metal ions coexisting. This work develops a new approach to retrieve valuable metals from aqueous solution or e-wastes. [30] The typical novel redox fuel cells developed in our lab are briefly shown in Table 3.

Table 2. Brief summary of unconventional oxidants of liquid fuel cells

Species	Cathodic reaction	Standard redox potential (E ⁰)
Cr(VI)	$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	1.33 V
Au(III)	$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$	1.52 V
Ag(I)	$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	0.799 V
	$\text{Ag}(\text{NH}_3)_2^+ + \text{e}^- \rightarrow \text{Ag} + 2\text{NH}_3$	0.373 V
Cu(II)	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	0.337 V
Nitrate	$2\text{NO}_3^- + 12\text{H}^+ + 10\text{e}^- \rightarrow \text{N}_2 + 6\text{H}_2\text{O}$	0.74 V

Table 3. Brief summary of unconventional coupled redox fuel cells in our study

Redox pair	Anodic catalyst	Cathodic catalyst	OCV (V)	Maximum power density (mW m ⁻²)
urine/Cr(VI)	Ni/C	none	1.3	3400 [26]
phenol/Cr(VI)	Ni/C	none	~1.1	184 [27]
urea/Cr(VI)	Ni/C	none	1.56	- [31]
ethanol/Cr(VI)	Pt/C	none	1.46	1900 [32]
ethanol/Au(III)	Pd ₂ Ni ₃ /C	none	1.40	- [30]
ethanol/Ag(I)	Pd ₂ Ni ₃ /C	none	0.95	- [30]
ethanol/Cu(II)	Pd ₂ Ni ₃ /C	none	0.96	- [30]
NaBH ₄ /Cu(II)	Ni/C	none	1.65	7200 [29]
ammonia/nitrate	Pt/C	Pd/C	0.66	170 [28]

4. PROSPECT

Energy extraction from H-rich small molecules can be successfully achieved via direct liquid fuel cells under non-precious transition metal catalysts to generate electricity under atmospheric conditions. The assembly of a DLFC same as common fuel cell requires fuels to provide electron and electron acceptor of oxygen or air as oxidant. Under the action of catalyst, oxygen receives electrons transferred from anode to produce reduction reaction, and generates current under external load. Except for the oxygen, pollutants like heavy metals can services as electron acceptor and wastes such as urea or phenol acts as fuel and then both pollutants can be removed or even recovered.

DLFC exhibits the feasibility to generate electricity but also it can be applicable. Regarding the state of the art for DLFC investigations, more attention would be paid how to increase current density of fuel output. Hence, mechanistic study would be a priority including reaction kinetics

ACKNOWLEDGEMENT

This work is supported by the National Natural Science Foundation of China (No. 21473158).

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