A review on unitized regenerative fuel cell technologies, part-A: unitized regenerative proton exchange membrane fuel cells

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Abstract

Energy storage and conversion is a very important link between the steps of energy production and energy consumption. Traditional fossil fuels are natural and unsustainable energy storage medium with limited reserves and notorious pollution problems, therefore demanding for a better choice to store and utilize the green and renewable energies in the future. Unitized regenerative fuel cell (URFC), a compact version of regenerative fuel cell with only one electrochemical cell, is one of the competent technologies for this purpose. A URFC can produce hydrogen fuel through an electrolysis mode to store the excess energy, and output power in a fuel cell mode to meet different consumption requirements. Such a reversible system possesses several distinctive advantages such as
high specific energy, pollution-free, and most importantly, the decoupled energy storage capacity with rated power. Based on the different electrolytes utilized, current available URFC technologies include the most common proton exchange membrane (PEM)-based URFC, and other types of URFC such as the alkaline, solid oxide and microfluidic URFCs. This part of the URFC review emphasizes on the PEM-based URFC. Specifically, the research progress on both cell components and systematic issues is introduced. Benefiting from its fairly mature technology stage, the PEM-based URFC has already been applied in aerospace and terrestrial areas. However, for large-scale application, their cost and efficiency are still the obstacles when competing with other energy storage technologies. As for the alkaline, solid oxide and microfluidic types of URFC, their research progress is reported independently in part B of this review.

**Keywords**

Unitized regenerative fuel cell, proton exchange membrane, bifunctional catalyst, gas diffusion layer, bipolar plates, practical applications

**Abbreviations**

ATO: Sb-doped SnO$_2$

BHC: Bifunctional hydrogen catalyst

BOC: Bifunctional oxygen catalyst

BOP: Balance of plant

BPPs: Bipolar plates

EC: Electrolysis cell
FC: Fuel cell
GDB: Gas diffusion backing
GDE: Gas diffusion electrode
GDL: Gas diffusion layer
HER: Hydrogen evolution reaction
HOR: Hydrogen oxidation reaction
LLNL: Lawrence Livermore National Laboratory
MEA: Membrane electrode assembly
MH: Metal hydride
MPL: Microporous layer
OER: Oxygen evolution reaction
ORR: Oxygen reduction reaction
PEM: Proton exchange membrane
PEMEC: Proton exchange membrane electrolyzer cell
PEMFC: Proton exchange membrane fuel cell
PPD: Peak power density
PV: Photovoltaic
RFC: Regenerative fuel cell
RFB: Redox flow battery
R-PEMFC: Regenerative proton exchange membrane fuel cell
UPS: Uninterrupted power supply
URFC: Unitized regenerative fuel cell
UR-PEMFC: Unitized regenerative proton exchange membrane fuel cell
UR-AFC: Unitized regenerative alkaline fuel cell  
UR-SOFC: Utilized regenerative solid oxide fuel cell  
UR-MFC: Utilized regenerative microfluidic fuel cell  
ZEV: Zero-emission vehicles

1. Introduction

Nowadays environmental issues, such as global climate change and air pollution, have strongly attracted world’s attention. Traditional fossil fuels are still the predominant energy source for human activity, which are responsible for many well-known environmental problems, typically the global warming due to massive CO₂ emissions and the air pollution due to the emissions of SOₓ and NOₓ. In addition, fossil fuel reserves are limited. According to a prediction in 2009, coal can last for about 107 years, crude oil for about 35 years, and nature gas for about 37 years [1], while world population and energy demand still keep increasing. When facing these problems, either the optimization of existing fossil fuel utilization facilities or the development of renewable energy sources is promising, of which the latter one is more sustainable considering the limited reserve of fossil fuels. Renewable energies such as solar, wind, geothermal etc. are getting more and more attention and investment in recent years, with a growing capacity and proportion in world energy supply. However, the intermittent nature of renewable energies has restrained their application prospect. In order to balance with their energy production intermittency, either secondary batteries or regenerative fuel cells (RFC) are proposed as auxiliary energy storage & conversion component for them.
As shown in Figure-1(a), a RFC is composed of three main parts: a fuel cell for power generation, an electrolysis cell for fuel production, and a fuel storage component. In addition, an oxygen storage part can also be added for a completely-closed RFC system. When coupled with renewable power sources, the electrolyzer can utilize the redundant and inferior power input to split water for hydrogen generation, while during the power output period hydrogen fuel will flow back to fuel cell and output stable electric power. To make a more compact system, the fuel cell part and the electrolyzer part can be unitized into a single electrochemical cell, which functions alternatively as fuel cell and electrolyzer, as shown in Figure-1(b). This unitized regenerative fuel cell (URFC) holds several advantages against the conventional discrete RFC, such as lower capital cost, simpler structure, higher specific energy, no need for auxiliary heating [2], etc.

Till now, secondary batteries are widely used for energy storage purpose due to their high round-trip efficiency (around 80%) [3], but their drawbacks are also evident. The durability of secondary batteries is not very satisfactory when facing deep cycling, and their specific energy is constrained by the heavy weight. Moreover, the coupling of energy storage capacity and rated power has made secondary batteries less efficient to scale up. To solve this problem, redox flow batteries (RFBs) are proposed as an alternative choice. Unlike the conventional secondary batteries which store reactants within the cell, the RFBs utilize electro-chemical reactants dissolved in electrolytic solutions which are stored in external tanks and circulated on the electrode surface during operation. In this way, the energy storage capacity and rated power of RFBs are decoupled [4]. By enlarging the electrolyte storage tank the capacity can be easily increased, while the rated power can be enhanced by enlarging the electrodes’ area or
through stacking. However, due to the bulk electrolyte solution contained in the system, the specific energy of RFBs is generally much lower. Similar to RFBs, URFCs also store the fuel and oxidant, generally H₂ and O₂, externally in separated gas tanks, therefore achieving decoupled storage capacity and output power, but their specific energy is much higher due to the absence of liquid electrolyte, which is about 0.4 to 1.0 kWhkg⁻¹ including the mass of the hydrogen and oxygen gas tanks [5]. In addition, URFCs can be totally charged and discharged without damaging the durability compared with secondary batteries. These advantages have made URFCs very competitive against secondary batteries and RFBs. However, URFCs generally achieve lower round-trip efficiency than batteries due to the sluggish oxygen reactions. Other issues such as high cost, hydrogen storage, and relatively low technology readiness, have also hindered their applications.

Same as the classification of fuel cells, URFCs can also be classified by the electrolytes they employ, such as the unitized regenerative proton exchange membrane fuel cell (UR-PEMFC), unitized regenerative alkaline fuel cell (UR-AFC), utilized regenerative solid oxide fuel cell (UR-SOFC) and utilized regenerative microfluidic fuel cell (UR-MFC). The principal difference among these different types of URFC exists in the electrolyte where different ions are transferred to connect the oxidation and reduction reactions. Figure-2 gives the schematic diagrams of different types of URFC operated in both modes. The conducting ions in the electrolyte are H⁺ and OH⁻ for UR-PEMFC and UR-AFC, respectively, while for UR-SOFC two different ions, i.e. O²⁻ and H⁺, can both be utilized. As for UR-MFC, it is not included in this figure due to its flexible electrolyte choice. In addition, Table-1 gives a brief comparison of different URFC technologies, including their main feature, working temperature, efficiency, and R&D status.
In this part of review, recent research progress on UR-PEMFC is reported first, which is currently the most-developed URFC technology. Research works on different cell components will be introduced separately, from the inner component, i.e. the bifunctional catalysts, to the outermost component, i.e. the bipolar plates. In addition, systematic issues such as electrode configuration, fuel cell stacking, heat and water management, etc. are also presented. With all these efforts, UR-PEMFCs have already achieved an early application stage in many areas, including aerospace and aviation, renewable energy, power supply, and transportation. which are also introduced at the end of this review. As for the other URFC technologies, detailed report will be given in part-B of this review.

2. Unitized regenerative proton exchange membrane fuel cell (UR-PEMFC)

Proton exchange membrane fuel cell (PEMFC) is one of the most developed fuel cell technologies with abundant R&D efforts, since its first appearance in the early 1960s by Willard Thomas Grubb and Leonard Niedrach of General Electric [6]. It can convert chemical energy contained in fuels such as hydrogen, methanol, ethanol etc. directly into electrical energy under mild reaction conditions, i.e. 20-100°C and moderate pressure. The reverse of this reaction to produce hydrogen fuel by water electrolysis is also possible with the device called proton exchange membrane electrolysis cell (PEMEC), which was proposed at nearly the same time with PEMFC [7]. One possible way to utilize these two devices is to combine them into a single system, namely the regenerative proton exchange membrane fuel cell (R-PEMFC), which can store excess energy as hydrogen fuel by the electrolysis cell component and output electrical energy by the fuel cell component. To make the system simpler and more compact, the PEMFC component
and the PEMEC component were further integrated into one bifunctional electrochemical cell, i.e. the unitized regenerative proton exchange membrane fuel cell (UR-PEMFC), which was first put forward in the early 1960s [8] and successfully tested for space missions in 1973 [9].

Since its first appearance, UR-PEMFC has earned numerous interests because of its distinct advantages over other energy storage technologies. With much higher specific energy (0.4-1.0 kWhkg⁻¹ [5]), long-term storage ability due to the elimination of self-discharge, and most importantly, the decoupling between power output ability and energy storage ability, UR-PEMFC is deemed to be promising for practical applications. In the late 1990s, Mitlitsky et al. [5, 10-12] from the Lawrence Livermore National Laboratory (LLNL) have done great works to improve cell performance and cycle stability of UR-PEMFCs with a relatively low catalyst loading (1mgcm⁻²). Negligible degradation was observed for 2010 cycle tests. Light-weight pressure vessel was also designed to improve the systematic specific energy. As for commercial applications, Proton Energy Systems, Inc. has developed their product UNIGEN™ which performed identically to dedicated electrolyzers in electrolysis cell (EC) mode and to dedicated fuel cells in fuel cell (FC) mode [13]. Despite of these great efforts, UR-PEMFC technology has still not ushered large-scale commercial application stage. Continuous efforts have been made to further improve their performance, cycle stability, round-trip energy efficiency and cost-effectiveness.

This section will mainly introduce recent research progress on different UR-PEMFC components, including bifunctional hydrogen catalyst (BHC), bifunctional oxygen catalyst (BOC), gas diffusion layer (GDL), and bipolar plates (BPPs). Moreover, research
works on electrode configuration, single cell stacking, and other systematic issues such as heat & water management will also be reported. Considering the commonly employed commercial Nafion membrane in UR-PEMFCs, membrane development is not included in this review. Table-2 has summarized the existing UR-PEMFC prototypes demonstrated to date in the literature, with both their cell parameters and performance specified, such as the catalyst/electrolyte/GDL material, operation temperature, peak power density (PPD), round-trip efficiency, and cycle stability. Figure-3 gives a schematic diagram of the main components in a UR-PEMFC single cell, including a Nafion membrane successively sandwiched by the catalyst layer, GDL and BPPs. In addition, micrographs of the catalyst dispersion on catalyst support, catalyst layer structure, GDL micro structure, and commercial BPPs are also included in this figure.

2.1 Bifunctional hydrogen catalyst (BHC)

Pt has long been utilized and is still the most efficient and stable BHC for UR-PEMFCs. Great efforts have been made to decrease its loading to less than 0.5mgcm$^{-2}$, considering the scarcity and high cost of Pt [14-20]. However, for large-scale applications, noble metal-free catalysts are still preferred to replace Pt. Goff et al. [21] grafted nickel catalyst on carbon nanotubes to mimic the active sites of hydrogenase enzymes. This synthetic catalyst not only resulted in low overvoltage (20mV) in hydrogen evolution reaction (HER) and excellent stability (over 100,000 turnovers), but also exhibited high efficiency for hydrogen oxidation reaction (HOR) with comparative current densities to the hydrogenase-based materials. Andrews et al. [22] built up a novel UR-PEMFC prototype called the “proton flow battery” with an integrated metal hydride (MH) as
hydrogen electrode. This MH electrode can not only catalyze the HOR and HER, but also store the generated hydrogen fuel in the form of “proton”, thus eliminating both the Pt catalyst and the outside hydrogen storage component. However, its cell performance and hydrogen storage capacity are yet to be improved.

2.2 Bifunctional oxygen catalyst (BOC)

As shown in Figure-3, the BOC layer lies between the PEM and the GDL, and is directly responsible for both oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). Competent BOCs should have such properties as high catalytic activity, long-term durability, high electronic conductivity and low cost. Currently, the choice of BOCs in UR-PEMFCs is still limited to noble metal catalysts. Various research works have been done to improve their properties, including both the optimization of catalyst composition and catalyst support. In 2006, Pettersson et al. [23] have published a review paper focusing primarily on BOC development. Based on their work, this section will add more recent related research works ever since.

2.2.1 Catalyst composition:

To date, most of the BOCs utilized in UR-PEMFCs are still noble metal-based by the combination of platinum (Pt), ruthenium (Ru), iridium (Ir) and their oxides. Pt, the preferred catalyst for ORR, is not suitable for OER, while the preferred catalysts for OER such as Ru, Ir and their oxides are not suitable for ORR. Therefore, a compromise is made by combining Pt with Ru, Ir or their oxides as composite BOCs.
Research works have been carried out to figure out the best catalyst combination for BOC. Chen et al. [24] screened 715 unique combinations of five elements (Pt, Ru, Os, Ir, and Rh) to evaluate their activity and stability as BOC. They found that the Pt-Ru rich region of the Pt-Ru-Ir ternary exhibited high activity towards ORR/OER with good anodic corrosion resistance, among which the Pt\textsubscript{4.5}Ru\textsubscript{4}Ir\textsubscript{0.5} is more active than Pt\textsubscript{1}Ir\textsubscript{1}. This conclusion was also confirmed by Rivas et al. [25]. Yim et al. [26, 27] screened several composite catalysts including Pt, Pt-Ir, Pt-RuO\textsubscript{x}, Pt-IrO\textsubscript{x}, Pt-Ru and Pt-Ru-Ir. They found that the FC performance was in the order of Pt black > Pt-Ir > Pt-RuO\textsubscript{x} > Pt-Ru ~ Pt-Ru-Ir > Pt-IrO\textsubscript{x}, while the EC performance was in the order of Pt-Ir ~ Pt-IrO\textsubscript{x} > Pt-Ru > Pt-Ru-Ir > Pt-RuO\textsubscript{x} ~ Pt black, among which the Pt-Ir possessed the best cycle performance and highest round-trip efficiency. As for Pt\textsubscript{4.5}Ru\textsubscript{4}Ir\textsubscript{0.5}, they found that its activity was just similar to Pt-Ru, which was contradictory to Chen and Rivas’s findings [24, 25]. Regardless of this divergence, Ru and its oxides are found to be unstable under the operating conditions [28]. Therefore, the combination of Pt and Ir or its oxides is currently the mainstream choice for BOC. Various investigations towards their elemental ratio, catalyst preparation method, microstructure etc. have been conducted. In addition, a recent related review by Antolini et al. [29] has introduced Ir as catalyst and co-catalyst for ORR/OER.

As shown in Table-2, there seems no specific optimal ratio between Pt and Ir, of which the proportion of Ir (or IrO\textsubscript{2}) can range from 1wt.% to 50wt.% in different studies. This divergence might be due to the different catalyst/electrode preparation methods in different studies. In general, the proportion of Pt should be more than half, due to the incapability of Ir towards ORR. As for the preparation of composite BOCs, mechanical
mixing is an easy and direct method that is commonly employed, which however cannot finely disperse the different catalyst components, so agglomeration tends to happen after the mixing. To solve this problem, different synthesize methods were developed instead of direct mixing, including Pt deposited on IrO$_x$ [20, 30], IrO$_x$ deposited on Pt [15, 31, 32], or a further mixture after catalyst deposition [19, 33, 34], all of which were reported to obtain a better bifunctional performance than the mixed Pt-IrO$_x$ catalyst. Figure-4 also gives a graphic description of the above-mentioned deposited BOCs. In general, by depositing one catalyst component on the surface of the other, better particle dispersion and less agglomeration can be achieved, leading to enhanced electrochemical active surface area and electronic conduction for the BOC.

2.2.2 Catalyst support:

Catalyst support plays very important roles in electro-catalysis. First it provides a physical surface for the catalyst particles to disperse on, leading to a larger catalyst surface area and therefore higher electro-catalysis rate. The catalyst loading can also be lowered down with catalyst support. Moreover, catalyst support helps to control the wettability and provide better electronic conductivity for the electrode. A good catalyst support should have such features as high surface area, good electronic conductivity, high corrosion resistance, and low cost. For PEMFC, carbon black is commonly used as catalyst support in both hydrogen and oxygen electrode, which is no longer suitable in UR-PEMFCs especially on the oxygen side. This is due to the fact that the high anodic potential at the BOC in EC mode will cause severe carbon corrosion via the following
reaction [35], which is, unfortunately, accelerated by the dispersed catalyst on electrode surface.

\[
C + 2H_2O^{\text{Pt}} \rightarrow CO_2 + 4H^+ + 4e^- \quad (E_0 = 0.118V \ vs.\ RHE \ at \ 25^\circ C)
\]

Efforts have been made to develop suitable catalyst support for the BOC in UR-PEMFCs. One possible choice is to use a portion of the catalyst itself as support, as mentioned in Section 2.2.1. However, the surface area provided by either Pt or IrO₂ is not high enough, and it is also not cost-effective to use noble metals as catalyst support. Instead, non-noble metal-based supports such as titanium oxides, titanium carbides, graphitized carbon etc. have been proposed, which is summarized in Table-3. Titanium oxides are considered to be promising as UR-PEMFC catalyst support [18, 36], whose performance can be further improved by niobium-doping [37-39]. In addition, titanium carbide (TiC) and nitride (TiN) have also been investigated [40-43], among which the TiCN-supported catalyst has demonstrated remarkable catalytic activity and corrosion resistance [42, 43]. However, particle agglomeration was found to be aggravated with higher nitrogen content in these catalyst supports [43]. Other catalyst support materials were also found to be suitable in UR-PEMFCs, such as the graphitized carbon [44] and Sb-doped SnO₂ [45].

2.3 Electrode preparation

After synthesizing bifunctional catalysts, different methods have been proposed to fabricate the electrode. Traditional roll press method uses PTFE to bond the catalyst
powder into a self-standing porous electrode, which however would lead to a high catalyst loading up to 10mg cm$^{-2}$ [31, 46] and a poor mass transport due to the thick electrode. To reduce the catalyst loading, paste method, also called the decal method or transfer printing method, is proposed which uses a PTFE sheet to support the thin film electro-catalyst before pasting it onto the membrane. Catalyst loading can be decreased to 2-4mgcm$^{-2}$ [47], and could even reach 0.4mgcm$^{-2}$ [14]. To use this method, a catalyst ink or slurry is prepared first by mixing the catalyst with Nafion solution and isopropanol, and then dispersed by ultrasonic treatment. The Nafion plays the role of catalyst binder while the isopropanol is used for better catalyst dispersion. In addition to the paste method, the catalyst ink can also be applied directly onto the membrane or GDL by either brushing [15-17] or spraying [18-20]. Other methods such as screen printing [48] and chemical reduction [49] have also been proposed in the literature.

2.3.1 Catalyst binder

Nafion is commonly used as catalyst binder when preparing electrodes. It plays important roles in providing proton conductivity between catalyst and membrane, adhesion of catalyst on membrane/GDL, and catalyst uniform dispersion. However, commercial Nafion binder has several problems such as brittleness, low proton conductivity, and vulnerable to alcohols [50]. Jung et al. [50] modified the Nafion binder by using dimethylacetamide as dispersion solvent, and compared its property with commercial Nafion binder. The modified Nafion binder showed much lower dissolution in methanol solution, higher proton conductivity and better water uptake than the commercial one. When applied in a UR-PEMFC, more stable performance was achieved
in both FC and EC mode. UR-PEMFCs with Nafion binder can also get flooded easily at high current densities in FC mode due to the high hydrophilicity of Nafion. In order to improve the water management and mass transport in FC mode, Chen et al. [51] developed a novel membrane electrode assembly (MEA) by the Nafion-pyrolyzed method. The Nafion binder used in the oxygen electrode was pyrolyzed in nitrogen at 320°C for an hour before the MEA was formed. UR-PEMFC with this novel MEA exhibited a high water electrolysis performance and a much higher fuel cell performance than that of the conventional MEA. Fuel cell efficiency and round-trip efficiency is improved by 13.5% and 10.8% at 700mAcms² compared with the cell with normal Nafion binder.

2.3.2 Catalyst layer structure

The effect of different catalyst layer structures on cell performance and stability has also been investigated in the literature. Liu et al. [52] proposed a composite electrode with an extra layer of catalyst applied on the GDL, which improved the UR-PEMFC stability and cycle life for over 25 cycles. Wittstadt et al. [53] investigated the effect of different modifications to MEA especially on the oxygen side. By sputtering extra Pt onto the BOC, the MEA achieved better performance in both modes. By sputtering extra Pt directly onto the membrane (oxygen side), impermeability of the MEA was improved which leads to a higher potential at low current density region, but the power density at high current density was reduced due to the weakened contact between electrode and electrolyte. Chen et al. [54] investigated the effect of different catalyst layer structures on UR-PEMFC performance and round-trip efficiency. The highest round-trip efficiency was achieved by the structure of “Pt sprayed on GDL and then IrO₂ sprayed on Pt”, while
the lowest efficiency was achieved by the structure of “Pt sprayed on membrane and IrO$_2$ sprayed on GDL”. Altmann et al. [55] also investigated various BOC layer structures, including single catalyst layer of Pt-IrO$_2$ mixture, multilayered Pt and IrO$_2$, and segmented catalyst layer of Pt and IrO$_2$, as shown in Figure-5. It was found that the single layer structure performed the best among the three different structures.

2.4 Gas diffusion layer (GDL)

As shown in Figure-6(a), a gas diffusion layer (GDL) generally consists of two parts: a thin and porous substrate called gas diffusion backing (GDB), and another porous layer coated on GDB called microporous layer (MPL). The GDB provides supporting substrate and gas channels for the electrode, while the MPL helps in water management and mass transport by modifying the pore structure of GDB. In some cases, the catalyst is directly deposited on GDL to form a gas diffusion electrode (GDE), as shown in Figure-3.

Table-4 has summarized the existing GDL materials suitable for working in UR-PEMFCs. For PEMFCs, hydrophobic carbon paper or carbon cloth is commonly adopted as GDB because of its high electronic conductivity, low cost and easy processing. However, such kind of GDB is no longer suitable for UR-PEMFCs because of the severe carbon corrosion in EC mode and the required balance between hydrophilic and hydrophobic properties of the GDB [56]. Instead, titanium material is proposed as a promising candidate for GDB because it is highly conductive and corrosion-resistant even under high-potential and acidic environment. Both bare Ti-felt GDB [53, 56-59] and Ti-felt GDB coated with Ti-powder MPL [60, 61] have been applied in UR-PEMFCs, as shown in Figures 6(b) and 6(c), respectively. It is found that by adding an appropriate
amount of PTFE into the Ti-felt GDB, both cell performance and stability can be improved [53, 56], while a larger fiber diameter of Ti-felt can harm the EC performance but improve the FC performance [57, 58]. By coating Ti-powder MPL to Ti-felt GDB, EC performance is not affected, but FC performance is significantly improved under fully humidification condition attributed to the hydrophobic meso-pores in GDL brought by the Ti-powder, which can improve mass transport in FC mode [60, 61].

Even with so many advantages, titanium GDB can also be oxidized in EC mode and form a low-conductive oxide surface layer, leading to an elevated cell resistance. Moreover, titanium material is quite expensive, and it is difficult and costly to make it thinner, lighter and highly porous at present [62]. Conventional carbon paper can still be used as GDB in UR-PEMFCs if coated with a protective MPL, which can combine the active oxygen species (oxygen atom and hydroxyl free radicals [63, 64]) to form oxygen molecules rapidly before they diffuse to the carbon GDB and corrode it. Such MPL is generally composed of an OER-active component (Ir or IrO$_x$) and a corrosion-resistant component (Ti or TiO$_x$), such as the Ti-powder supported IrO$_2$ [65], IrTiO$_x$-doped TiC [62], Ir-TiN composite [66], etc. In addition, graphitized carbon MPL is also proved to be able to improve the stability of the carbon paper GDB [16].

### 2.5 Bipolar plates (BPPs)

As the outermost cell component, BPPs support the MEA for single cells and serve as separator for the stack. In addition, BPPs also help in fuel & oxidant distribution, current collection, and heat and water management [67-72]. Competent BPPs should have such properties as non-permeability, high thermo-conductivity, low interfacial contact
resistance, good mechanical strength, high corrosion-resistance, lightweight, cost-effectiveness, etc. [67-72]. A more specific review paper on suitable BPPs for UR-PEMFC has been published by Dihrab et al. [73] in 2009.

Three candidate materials have been proposed for BPPs in the literature: graphite, polymer blended with carbon, and metal [72]. Graphite is commonly used as BPPs in PEMFCs because of its excellent electrical conductivity, high chemical stability, and good hydrophobicity, but its shortcomings are also evident, including poor mechanical strength and manufacturability. As for UR-PEMFCs, the high positive overpotential in EC mode and the acidic environment can cause severe corrosion to graphite BPPs, leading to not only a weakened electrical contact between electrodes and BPPs but also a decreased BPPs hydrophobicity, which can increase the ohmic resistance and mass transport losses. Using polymer blended with carbon can improve the poor manufacturability of graphite, but suffers from weakened electrical conductivity. Instead of carbon-based materials, metal-based BPPs are proposed as a good alternative because of their high mechanical strength, non-permeability, excellent manufacturability and cost-effectiveness. The metal includes titanium, stainless steel, aluminum, copper alloy, nickel, etc.

Table-5 summarizes the suitable BPPs for UR-PEMFCs. Titanium BPPs have been extensively investigated for UR-PEMFCs because of their excellent corrosion resistance and light weight, which, however, suffer from passivation problem due to the titanium oxide layer formed on their surface under oxidation environment. The same problem also occurs for stainless steel BPPs. Therefore, surface modification is needed in order to further improve their corrosion resistance. Jung et al. tried both Au-coated [67] and Pt-
coated [68] Ti BPPs for UR-PEMFC, which achieved much better stability than the carbon-based BPPs. As shown in Figure-7, the Au-coated Ti-BPPs exhibited much better stability than the carbon-based BPPs with a 5 times lower voltage degradation rate. Nevertheless, Au or Pt coating can be quite expensive considering the high surface area of BPPs. To lower down the cost, Ti-Ag film [69], Ti-Ag-N film [71], or (Ti,Zr)N coating [72] was utilized instead, which can also improve the cycle stability of UR-PEMFCs.

Apart from corrosion resistance improvement, flow channel optimization is another important aspect for BPPs, in order to achieve a better management of fuel, oxidant and water. Hwang et al. [70] compared three different flow channels of BPPs on the oxygen side, including the serpentine-single shape, serpentine-dual shape, and parallel shape as shown in Figure-8. It was found that the serpentine-single flow channel can achieve the highest FC performance and comparable EC performance among the three channel shapes.

2.6 Electrode configuration

All the above-mentioned research works deal with the UR-PEMFC with the so-called “H₂ and O₂ electrode configuration”, which is currently the mainstream of UR-PEMFC research. With this configuration, each electrode will deal with the same reactant, namely the BHE and BOE as shown in Figure-9(a). In addition to this configuration, Figure-9(b) shows another type of UR-PEMFC which utilizes the same electrode to deal with the same redox reaction, which means that the “oxidation electrode” deals with OER and HOR, while the “reduction electrode” deals with ORR and HER [74-77]. This is called
the “reduction and oxidation electrode configuration”. The “H₂ and O₂ electrode configuration” has the advantage of simple gas management. However, carbon-based material is no longer suitable on the oxygen side due to carbon corrosion under the EC mode, and less efficient ORR catalyst (i.e. Pt-IrOₓ composite catalyst) has to be utilized rather than Pt, leading to a compromised FC performance. The advantage of the “reduction and oxidation electrode configuration” is that conventional PEMFC components such as Pt catalyst and carbon-based materials can be directly utilized on the cathode side, but the gas compartments need to be purged every time before mode switching.

2.7 Stacking

The energy storage rate and power output ability of a single cell is normally insufficient to satisfy practical demands due to its limited cell voltage and electrode area. Hence, it is necessary to stack multiple UR-PEMFC single cells together in series or in parallel to improve the fuel generation rate and power level. Figure-10 shows some stack prototypes demonstrated in the literature, including both commercial products from Proton Inc. [11], LLNL [11], Lynntech, Inc. [78], and in-lab products by Sone [79], Grigoriev et al. [80], and Millet et al. [81]. Table-6 also summarizes the main features and stack performance of the demonstrated UR-PEMFC stacks in the literature, including both single cell parameters and stack designs. In addition, more details on UR-PEMFC stack development can be found in a recent review by Gabbasa et al. [82]

Su et al. [83] designed a planar 6-cell UR-PEMFC stack (in series) as a mini power source. Under the EC mode, the hydrogen generated can be stored in a hydrogen storage
alloy and provide fuel for the subsequent FC mode operation. Test results showed an OCV of 4.9V and a maximum power density of 74.8mWcm$^{-2}$ for this stack. As for durability, the stack can only work under 20mAcm$^{-2}$ for 40min due to the limited hydrogen storage capacity. Cycle test showed that the stack voltage was constant during 10 cycles of operation. Sone [79] demonstrated a 100W-class URFC stack prepared by Takasago Thermal Engineering Co., Ltd. This URFC stack had 17 cells in series. In FC mode the nominal current level was 15A at 12V, and in EC mode the nominal current was less than 30A at 28V. Moreover, the performance of each single cell was very uniform in both working modes: the difference in cell voltage was within 20mV when operated at 40~60℃. Grigoriev et al. [80] developed a 7-cell UR-PEMFC stack based on the “reduction and oxidation electrode configuration”. Tested under 80℃, nominal electric power consumption of 1.5kW in EC mode and nominal electric power production of 0.5kW in FC mode is achieved. At 0.5Acm$^{-2}$, the mean cell voltage is 1.74V in EC mode and 0.55V in FC mode, leading to a 30% round-trip efficiency. In the GenHyPEM project (2005-2008), a 2-cell UR-PEMFC stack, also based on the "reduction and oxidation electrode configuration", was developed by Millet et al. [81]. Performance of this UR-PEMFC stack in both modes are very close to the data measured on individual fuel cell and electrolysis devices, but the long-term stability under alternative operation in FC and EC modes is still not sufficiently good.

2.8 System-level development considerations

As shown in Figure-11, an integrated UR-PEMFC system is much more complicated than the stack alone, including other auxiliary components such as gas storage, pressure
control, water storage, heat pipe, system control interface, etc. [84] Therefore, in addition to single cell and stack optimization, other system-related issues also need to be carefully considered, among which the heat and water managements are especially important to ensure a stable operation of the UR-PEMFC system.

In order to maintain a constant working temperature in UR-PEMFCs, waste heat generated during FC and EC mode operation should be removed efficiently from the cell, which is generally accomplished by a heat exchanger or a radiator. However, such devices can lower down the system’s specific energy and cause parasitic power consumption. Instead of using external heat exchangers or radiators, loop heat pipes were employed which are coiled around gas tanks and covered with a thin layer of thermally conductive carbon composite, in order to transfer the waste heat from the cells to the gas tank surface as system radiator [84]. This novel heat exchanger is not only lightweight, but also consumes less parasitic power. Furthermore, it can also be applied as regenerative gas dryers/humidifiers (RGD/H) to dry the generated gases during EC mode operation, and humidify the reactant gases during FC mode operation [85].

Water management is another important issue in a UR-PEMFC system, which is, however, quite complicated. In general, a hydrophobic environment is needed in FC mode to prevent water flooding, while a hydrophilic environment is requisite in EC mode to provide sufficient water for the electrolysis reaction [47]. Therefore, a delicate balance between the proportion of hydrophobic PTFE and hydrophilic Nafion should be made in both the catalyst layer and the GDL, especially on the oxygen side where water is generated in FC mode and consumed in EC mode. Ioroi et al. [47] found that PTFE content can only affect the FC performance while Nafion content can affect both the FC
and EC performance. In conclusion, 5-7 wt.% PTFE and 7-9 wt.% Nafion were believed to be the most appropriate ratio. Jung et al. [16] concluded that 5wt.% PTFE in the electrode is optimum in terms of both cell performance and long-term stability. Zhuo et al. [86] found that the optimum amount of PTFE in the GDL (oxygen side) is 26.95% considering both FC and EC performance. These divergent conclusions might be due to the different catalyst compositions and different electrode structures employed in different research works, indicating that the appropriate ratio of PTFE and Nafion should be specifically tailored for a specific UR-PEMFC system. In addition to this, water content in the membrane electrolyte is also of great importance to its ionic conductivity, which is tightly coupled with cell thermal management. In general, the reaction heat should be removed efficiently from the MEA to prevent its temperature from elevating, e.g. by utilizing BPPs with high thermo-conductivity. Otherwise, the membrane electrolyte will get easily dehydrated, resulting in an elevated ohmic resistance and deteriorated cell performance.

3. Applications

As shown in Figure-12, URFCs can be potentially applied as energy storage & conversion devices in various areas, including aerospace and aviation, renewable energy, power supply, transportation, and portable applications. Among all these areas, URFCs are especially promising for aerospace applications. The mass of an aircraft is crucial and can be minimized by employing URFCs, benefited from their high specific energy. URFCs can also be integrated with solar/wind energies in remote off-grid areas. Considering their intermittency of electricity generation, URFCs can help solar/wind
energies to smooth their output, by storing solar/wind energy in EC mode and outputting stable electrical energy in FC mode. As for power supply, URFCs can either be employed as grid supplement to balance the different power demands during on-peak and off-peak periods, or as backup power/uninterrupted power supply (UPS) when off-grid. In addition, they are also popular in electric vehicle applications with zero emissions.

Till now, most of the reported URFC applications are based on UR-PEMFCs considering their higher technical maturity against other URFC technologies. However, due to their relatively high cost, most of current applications are still limited to aerospace and military fields. Similar to PEMFCs, the high cost of UR-PEMFC stacks is mainly resulted from the expensive cell components utilized, including the PEM, noble metal catalysts, GDL, and metal-based BPPs. Moreover, cost from the balance of plant (BOP) can constitute more than half in the total system cost, including the management cost of the fuel, oxidant, water, heat, etc. [87]. Furthermore, the continuous cycle operation of UR-PEMFCs between FC and EC mode can lead to a faster component degradation rate hence a shorter life time, which further raises their maintenance cost for component replacement. Therefore, UR-PEMFCs are mostly applied in high cost-tolerable areas at present. In order to promote their civil applications, novel cost-efficient substitutes are requisite in replacement of the expensive cell components, and the cost from BOPs should also be greatly lowered. In addition, their cycle stability should also be improved in order to achieve a much longer life time.

Nevertheless, tentative applications and studies of UR-PEMFCs for civil purposes, such as renewable energy, grid supplement and automobiles, are still available in the literature, which will be introduced in the subsequent sections. Due to the ambiguity
between RFC and URFC in some of the reports, both of them will be included considering the potentially available replacement of RFCs with URFCs.

3.1 Aerospace and aviation

Fuel cells such as PEMFCs and AFCs have long been applied in the field of aerospace as auxiliary power sources [88]. As for URFCs, additional electrolysis function is added to better satisfy the demands from different mission profiles, especially for geostationary satellites, solar aircrafts, and high altitude long endurance aircrafts [11]. Early in the 1960s, patent concerning UR-AFC for the Apollo program was filed by Ludwig [89]. In the 1990s, Mitlitsky et al. from the LLNL have published several reports on UR-PEMFCs for aerospace and aviation purpose [5, 10-12]. Afterwards, more and more applications of UR-PEMFCs in this area were reported.

In 2004, Connecticut-based Distributed Energy Systems have developed a multi-kWe capable, closed-loop, lightweight RFC for high-altitude airships, which can generate pressurized hydrogen and oxygen electrochemically without mechanical compression [90]. NASA Glenn Research Center has also demonstrated a closed-loop RFC for a solar electric aircraft in 2006 [91]. This RFC could store the input electrical energy and output a steady power of 5kWe for at least 8 hours. Its transition of different working modes was also demonstrated successfully. During 2010-2011, Japanese industrial conglomerate IHI, collaborated with Boeing company, produced a prototype RFC for aircrafts as auxiliary energy supplier of the engine generators [92]. This RFC can help optimize the aircraft electricity production, lowering the demand for energy supply and making the energy system much lighter.
For mission profiles with short discharge duration or low power requirement, secondary batteries still work better than URFCs so far, due to their higher efficiency and considering the disproportional mass of ancillary equipment in UR-PEMFCs to the mass of the spacecraft [93].

3.2 Renewable energy

In 2003, a collaborative Canadian project has developed a stationary 2kWe RFC system integrated with renewable energy such as photovoltaic (PV) or wind energy to generate sustainable hydrogen energy [94]. Maclay et al. [95, 96] developed a model which integrated RFC with a PV and battery system for solar-hydrogen powered residence application. It was found that by combining RFC with battery in the hybrid energy system, PV utilization, battery power density and efficiency, and the energy storage capacity were all increased. However, since RFCs generally operate at lower efficiencies than batteries, the overall system efficiency was decreased due to this combination. In the University of Zacatecas, Mexico, a 2.5kW hybrid energy system was developed for standalone application by Chavez-Ramirez et al. [97]. This hybrid system included a PV panel, a micro wind turbine, a UR-PEMFC and batteries. Control strategy for this system was also developed to achieve the highest performance and efficiency, by selecting which renewable source to feed the battery and which to meet the load demand autonomously. Raj et al. [98] compared the Standalone PV-diesel system with PV-H\textsubscript{2} system from economic point of view and found that a system with UR-PEMFC and metal hydride storage offered the most cost-effective solution.
3.3 Power supply

For power supply purpose, UR-PEMFCs can either be connected to the grid as peak shaver, or work independently as backup power/UPS. When connected to the main grid, UR-PEMFCs can utilize the redundant electricity from the grid during night time for hydrogen production and storage, while during the day time they can generate electricity back to the grid to deal with possible power shortage. Benefited from their decoupled power & capacity and long-term energy storage ability, UR-PEMFCs can effectively coordinate with local grid. For instance, Proton Energy Systems Inc. has built a 5kWe UR-PEMFC system for a telecoms site based on their product Unigen® [90]. During the on-peak period, this system can work as a peak shaver for the local grid and utilize the extra electric power to produce hydrogen.

As for off-grid power supplier, UR-PEMFCs are also very promising as backup powers or UPS for various applications, such as computers, data centers, telecommunication equipment [90], etc. The produced hydrogen can be stored for a long time without self-discharge, and the electricity supply capacity can be easily raised by increasing the hydrogen tank volume, resulting in a flexible backup power device for different missions. Proton Energy Systems Inc. has provided a 15kWe Unigen® UR-PEMFC system as backup power unit for the electric division of the Town of Wallingford in its control room battery system [99]. In the case of power failure, this system can use the high-pressure hydrogen to provide at least 8hrs of backup power at the rated load. Moreover, a 4kWe Unigen® URFC was also built as a UPS at Mohegan Sun Casino’s Energy, Environment, Economics & Education Center in 2005. [99].
3.4 Transportation

UR-PEMFCs have also been proposed for transportation applications such as the zero-emission vehicles (ZEVs) [11]. During the off-peak period, hydrogen fuel can be produced by connecting to the grid, while electricity can be provided to drive the electric motor during vehicle operation. Such a system eliminates the pollutions related to internal combustion engine-based vehicles, while retaining the quick refueling ability compared with battery-based vehicles, providing that hydrogen refueling infrastructure is mature. Unfortunately, the high price of present UR-PEMFCs has hindered their application in ZEVs. Instead, the URFC-battery-engine hybrid vehicles are proposed considering both the cost-efficiency and the possible reduction of gasoline consumption [100, 101]. Under this scheme, the battery pack is charged and hydrogen fuel is produced by a UR-PEMFC during the nighttime. When the vehicle works in the daytime, battery electricity is used first, then it is recharged by the UR-PEMFC with the stored hydrogen, and finally gasoline is consumed by the combustion engine. With this hybrid car, both the battery pack size and the power demand of the UR-PEMFC can be decreased, leading to a lower capital cost.

In addition to the ZEVs, UR-PEMFCs are also potentially applicable to other transportation applications such as buses, ships, airplanes, etc. as long as sufficient power is provided. However, this would be less cost-effective considering the high cost of UR-PEMFCs at present. Therefore, practical applications of UR-PEMFCs in these fields can hardly be found in literature.

4. Conclusion
This part of review has introduced the research progress on UR-PEMFC technology in detail. Great efforts on the development of different cell components are described singly, from the inner bifunctional catalysts, to the outmost BPPs. In addition, developments on several systematic issues such as electrode configuration, single cell stacking, and heat and water management are also presented.

UR-PEMFCs have shown their tremendous application prospect in areas of aerospace and aviation, renewable energy, power supply and transportation. Benefited from their high specific energy, deep cycling ability, and decoupled energy storage capacity with rated power, UR-PEMFCs have exhibited superior advantages for long-term energy storage and power output purposes. However, till now their application is still limited to aerospace and military fields due to their high-cost components such as noble metal catalysts, PEM, BPPs, and the cost from BOPs. Therefore, continuous research efforts are still needed to find cost-efficient substitutes, in order to realize their large-scale civil applications. Moreover, the round-trip efficiency and cycle stability of the present UR-PEMFCs also require further improvement to achieve higher competitiveness against other energy storage technologies.

Acknowledgements

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References:


Figure captions:

**Fig.1** Comparison between RFC and URFC: (a) RFC; (b) URFC.

**Fig.2** Schematic diagram of various URFC technologies operated in FC and EC modes: (a) UR-PEMFC; (b) UR-AFC; (c) UR-SOFC with oxygen ion conducting electrolyte; (d) UR-SOFC with proton conducting electrolyte.

**Fig.3** Composition of a typical UR-FEMFC single cell: (a) main cell components; (b) TEM micrograph of Pt supported on carbon [77]; (c) catalyst layer deposited on PEM [47]; (d) Carbon paper GDL [58]; (e) Commercial BPPs (from http://www.mgm-carbon.com/products/carbongraphitefelt/9.html)

**Fig.4** Various structures of the deposited Pt-IrO$_x$ composite BOCs: (a) IrO$_2$ deposited on Pt [31]; (b) Pt deposited on IrO$_2$ first and then mixed with Pt [19]; (c) Pt supported on Ir-deposited IrO$_2$ [33]; (d) Pt supported on IrO$_2$ [30]; (e) RuO$_2$ and IrO$_2$ supported on Pt [15]; (f) Ir@Pt nanodendrites [32]

**Fig.5** Various catalyst layer structures on the oxygen side [55]: (a) one-layer composite electrode; (b) multilayered electrode; (c) segmented electrode. (FC stands for fuel cell catalyst, i.e. Pt; EC stands for electrolysis cell catalyst, i.e. IrO$_2$)
**Fig. 6** GDL in UR-PEMFCs: (a) schematic diagram of the GDL structure; (b) Ti-felt GDB [61]; (c) Ti-felt GDB coated with Ti-powder MPL [61]

**Fig. 7** Stability of UR-PEMFC performance after running cell at 2.0V for 1 h every day [68], with: (a) carbon-based BPPs; (b) Pt-deposited Ti-BPPs.

**Fig. 8** Different flow channels of the BPPs on the oxygen side [70]: (a) serpentine-single channel; (b) serpentine-double channel; (c) parallel channel.

**Fig. 9** Two different electrode configurations for UR-PEMFCs: (a) hydrogen and oxygen electrode configuration; (b) reduction and oxidation electrode configuration.

**Fig. 10** UR-PEMFC stacks reported in the literature: (a) in-lab stacks by Sone [79], Grigoriev et al. [80], and Millet et al. [81] (From left to right); (b) Commercial stacks by Proton Inc. [11], LLNL [11], and Lynntech, Inc. [78] (From left to right).

**Fig. 11** UR-PEMFC systems: (a) a schematic model [84]; (b) a practical model [79]

**Fig. 12** Schematic representation of UR-PMFC applications in various fields (Figures of renewable energy, electric grid, laptop and cellphone from: http://all-free-download.com; Figures of space shuttle, satellite, airplane, cars, and UPS from http://openclipart.org)
### Table 1: Comparison between various types of URFC technology

<table>
<thead>
<tr>
<th>Types of URFC</th>
<th>Electrolyte</th>
<th>Main feature</th>
<th>Working temp. (°C)</th>
<th>Round-trip efficiency</th>
<th>Technical Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>UR-PEMFC</td>
<td>PEM</td>
<td>Noble-metal catalyst</td>
<td>20-100</td>
<td>40-50%</td>
<td>Mature</td>
</tr>
<tr>
<td>UR-AFC</td>
<td>Alkaline solution; AEM</td>
<td>Non-noble metal catalyst</td>
<td>20-120</td>
<td>30-40%</td>
<td>Developing</td>
</tr>
<tr>
<td>UR-SOFC</td>
<td>Proton-conducting ceramics;</td>
<td>High-temperature operation; High energy efficiency</td>
<td>500-1000</td>
<td>60-80%</td>
<td>Developing</td>
</tr>
<tr>
<td></td>
<td>Oxygen ion-conducting ceramics</td>
<td>Non-noble metal catalyst</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UR-MFC</td>
<td>Acid/Alkaline solution</td>
<td>Membraneless structure; Low capital cost</td>
<td>20-80</td>
<td>60% for vanadium-species</td>
<td>Early stage</td>
</tr>
</tbody>
</table>
### Table 2: Overview on various UR-PEMFC prototypes and their performances demonstrated to date

<table>
<thead>
<tr>
<th>References</th>
<th>BHC</th>
<th>Electrolyte</th>
<th>BOC</th>
<th>Temp. (°C)</th>
<th>PPD</th>
<th>Round-trip efficiency</th>
<th>Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shao et al. [14]</td>
<td>Pt 0.4mgcm⁻²</td>
<td>Nafion 115</td>
<td>Pt-IrO₂ (1:1 wt. ratio) 0.4mgcm⁻²</td>
<td>80</td>
<td>40.9% at 400mAcm⁻²</td>
<td>Stable for 4 cycles</td>
<td></td>
</tr>
<tr>
<td>Ioroi et al. [46]</td>
<td>Pt 8–10mgcm⁻²</td>
<td>Nafion 115</td>
<td>Pt-IrO₂ (10-30mol% IrO₂) 8–10mgcm⁻²</td>
<td>80</td>
<td>49% at 300mAcm⁻² 42% at 500mAcm⁻²</td>
<td>Stable for 10 cycles at 0.4 or 0.5Acm⁻²</td>
<td></td>
</tr>
<tr>
<td>Ioroi et al. [31]</td>
<td>Pt</td>
<td>Nafion 115</td>
<td>IrO₂/Pt (20at.% Ir₂O₃)</td>
<td>80</td>
<td>51% at 300mAcm⁻² 44% at 500mAcm⁻²</td>
<td>Stable for 4 cycles at 500mAcm⁻² (120hrs)</td>
<td></td>
</tr>
<tr>
<td>Ioroi et al. [47]</td>
<td>Pt 2–4mgcm⁻²</td>
<td>Nafion 115</td>
<td>Pt-Ir (10at.% Ir) 2–4mgcm⁻²</td>
<td>60</td>
<td>53% at 200mAcm⁻² 46% at 500mAcm⁻²</td>
<td>Stable for 3 cycles</td>
<td></td>
</tr>
<tr>
<td>Yim et al. [26]</td>
<td>Pt 4mgcm⁻²</td>
<td>Nafion 115</td>
<td>Pt-Ir (1:1 wt. ratio) 4mgcm⁻²</td>
<td>60</td>
<td>53% at 200mAcm⁻² 47% at 500mAcm⁻²</td>
<td>Stable for 4 cycles at 500mAcm⁻² (120hrs)</td>
<td></td>
</tr>
<tr>
<td>Yim et al. [27]</td>
<td>Pt 4mgcm⁻²</td>
<td>Nafion 115</td>
<td>Pt-Ir (99:1 wt. ratio) 4mgcm⁻²</td>
<td>60</td>
<td>53% at 200mAcm⁻² 47% at 500mAcm⁻²</td>
<td>Stable for 4 cycles at 500mAcm⁻² (120hrs)</td>
<td></td>
</tr>
<tr>
<td>Zhang et al. [15]</td>
<td>Pt/C 0.4mggcm⁻²</td>
<td>Nafion 115</td>
<td>(RuO₂–IrO₂)/Pt (25:25:50, wt. ratio) 2mgcm⁻²</td>
<td>80</td>
<td>50% at 400mAcm⁻² 43% at 500mAcm⁻²</td>
<td>Stable for 10 cycles at 0.4 or 0.5Acm⁻²</td>
<td></td>
</tr>
<tr>
<td>Jung et al. [16, 17]</td>
<td>Pt 0.5mgcm⁻²</td>
<td>Nafion 112</td>
<td>Pt-Ir (85wt.% Pt) 4mgcm⁻²</td>
<td>70–75</td>
<td>49% at 500mAcm⁻² 41% at 1Acm⁻²</td>
<td>Stable for 4 cycles at 500mAcm⁻² (120hrs)</td>
<td></td>
</tr>
<tr>
<td>Zhang et al. [19]</td>
<td>Pt/C 0.2mggcm⁻²</td>
<td>Nafion 212</td>
<td>Pt/IrO₂-Pt (5:95:10, wt. ratio) 1mgcm⁻²</td>
<td>80</td>
<td>1.16Wcm⁻²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Huang et al. [18]</td>
<td>Pt 0.5mgcm⁻²</td>
<td>Nafion 112</td>
<td>(Pt/TiO₂)-(Ir/TiO₂) (Pt/Ir=85/15 wt. ratio) 1mggcm⁻²</td>
<td>75</td>
<td>0.93Wcm⁻²</td>
<td>50.3% at 500mAcm⁻² 42.2% at 1Acm⁻²</td>
<td></td>
</tr>
<tr>
<td>Rivas et al. [25]</td>
<td>Pt/C 0.5–1mggcm⁻²</td>
<td>Nafion 115</td>
<td>Pt₃Ir₄Ru₁O₂₋₅ 3–5mgcm⁻²</td>
<td>80</td>
<td></td>
<td>FC performance decrease after WE operation</td>
<td></td>
</tr>
<tr>
<td>Cruz et al. [20]</td>
<td>Pt/C 0.3mggcm⁻²</td>
<td>Nafion 115</td>
<td>Pt-IrO₂ (1:1 wt. ratio) 0.5mgcm⁻²</td>
<td>Room temp.</td>
<td>0.1Wcm⁻²</td>
<td>47% at 50mAcm⁻² 37% at 100mAcm⁻² 30% at 200mAcm⁻²</td>
<td>Stable for 100hrs at 1.8V, with FC performance unchanged</td>
</tr>
<tr>
<td>Huang et al. [36]</td>
<td>Pt 0.5mgcm⁻²</td>
<td>Nafion 112</td>
<td>Pt/TiO₂</td>
<td>75</td>
<td>0.94Wcm⁻²</td>
<td>Very stable for 200hrs at 1.2V</td>
<td></td>
</tr>
<tr>
<td>Pai et al. [44]</td>
<td>Pt 0.25mggcm⁻²</td>
<td>Nafion 212</td>
<td>Pt/Graphitized carbon 0.25mgcm⁻²</td>
<td>190mWcm⁻²</td>
<td>37.5% at 100mAcm⁻²</td>
<td>Stable for 4 cycles at 100mAcm⁻² (56hrs)</td>
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</tr>
<tr>
<td>Cruz et al. [45]</td>
<td>Pt/C 0.4mggcm⁻²</td>
<td>Nafion 115</td>
<td>Pt-IrO₂ (1:1 weight ratio)/ATO 0.5mgcm⁻²</td>
<td>80</td>
<td></td>
<td>48% at 50Ag⁻¹ 43% at 100Ag⁻¹ 31% at 200Ag⁻¹</td>
<td>Acceptable stability for 400min at 0.6V in FC mode and 1.55V in EC mode, respectively.</td>
</tr>
<tr>
<td>Chen et al. [51]</td>
<td>Pt/C</td>
<td>Nafion 115</td>
<td>Pt-IrO₂ 2.1mggcm⁻² 0.9mggcm⁻²</td>
<td>80</td>
<td>474mWcm⁻²</td>
<td>60.3% at 100mAcm⁻² 52.1% at 300mAcm⁻² 44.2% at 500mAcm⁻² 37.8% at 700mAcm⁻²</td>
<td>Degradation rate of 0.6mVh⁻¹ at 2Acm⁻² in FC mode Degradation rate of 0.13mVh⁻¹ at 0.3Acm⁻² in</td>
</tr>
<tr>
<td>Jung et al. [50]</td>
<td>Pt 4mgcm⁻²</td>
<td>Nafion 112</td>
<td>Pt-Ir 4mgcm⁻²</td>
<td>70, 90</td>
<td></td>
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<td>Author(s)</td>
<td>Pt, mg/cm²</td>
<td>Pt, mg/g, cm²</td>
<td>IrO₂, mg/cm²</td>
<td>EC mode</td>
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<tr>
<td>Liu et al. [52]</td>
<td>Pt 0.8</td>
<td>Nafton 115</td>
<td>Pt-IrO₂ 2.2</td>
<td>Stable performance of 25 cycles (75hrs)</td>
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<td></td>
<td>mg/cm²</td>
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<td>1.7</td>
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<tr>
<td>Wittstadt et al. [53]</td>
<td>Pt 2</td>
<td>Nafton 117</td>
<td>Pt-Ir (1:1) 2</td>
<td>Better stability achieved with a PTFE-treated Ti GDL.</td>
<td></td>
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<tr>
<td></td>
<td>mg/cm²</td>
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<td>mg/g/cm²</td>
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<tr>
<td>Chen et al. [54]</td>
<td>Pt/C 0.5</td>
<td>Nafton 1035</td>
<td>Pt-IrO₂ 0.5</td>
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<tr>
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<td>mg/cm²</td>
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<td>mg/cm² 0.5</td>
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<td></td>
<td>mg/cm² 0.5</td>
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</tr>
<tr>
<td>Altmann et al. [55]</td>
<td>Pt 0.7</td>
<td>Nafton 1135</td>
<td>Pt-IrO₂ 0.7</td>
<td>Only short-term stability was achieved</td>
<td></td>
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<tr>
<td></td>
<td>mg/cm²</td>
<td></td>
<td>mg/cm² 0.7</td>
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<tr>
<td>Lee et al. [49]</td>
<td>Pt 0.38</td>
<td>Polypyrrole</td>
<td>Pt 0.38mg/cm²</td>
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<td></td>
<td>mg/cm²</td>
<td>Nafton</td>
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<td></td>
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<tr>
<td>Pettersson et al. [48]</td>
<td>Pt 3-4</td>
<td>Nafton 115</td>
<td>Pt-Ir 3-4</td>
<td>Stable for 3 cycles</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>mg/cm²</td>
<td></td>
<td>mg/cm² 3-4</td>
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<td></td>
<td>mg/cm² 3-4</td>
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<tr>
<td>Iorio et al. [56]</td>
<td>Pt 3-4</td>
<td>Nafton 115</td>
<td>Pt-Ir (85:15</td>
<td>GDB with 16mg/cm³ of PTFE coating achieved good stability for 4 cycles</td>
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<td></td>
<td>mg/cm²</td>
<td></td>
<td>atomic ratio)</td>
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<td></td>
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<td></td>
<td>3-4mg/cm²</td>
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<tr>
<td>Song et al. [65]</td>
<td>Pt/C 0.5</td>
<td>Nafton 112</td>
<td>Pt-IrO₂ (70wt. % Pt) 3mg/cm²</td>
<td>Stable for 20 cycles at 300mAcms⁻² (40hrs)</td>
<td></td>
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<tr>
<td></td>
<td>mg/cm²</td>
<td></td>
<td>mg/cm² 3</td>
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<td></td>
<td></td>
<td></td>
<td>mg/cm² 3</td>
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<tr>
<td>Chen et al. [62]</td>
<td>Pt/C 0.5</td>
<td>Nafton 112</td>
<td>Pt-IrO₂ (70wt. % Pt) 3mg/cm²</td>
<td>Stable for 15 cycles at 200mAcms⁻² (60hrs)</td>
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<tr>
<td></td>
<td>mg/cm²</td>
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<td>mg/cm² 3</td>
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<td></td>
<td>mg/cm² 3</td>
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<tr>
<td>Ito et al. [57, 60]</td>
<td>Pt</td>
<td>Nafton 115</td>
<td>Pt-IrO₂</td>
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<td></td>
<td>80</td>
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<tr>
<td>Hwang et al. [58, 61]</td>
<td>Pt</td>
<td>Nafton 115</td>
<td>Pt-IrO₂</td>
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<td>80</td>
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<tr>
<td>Huang et al. [66]</td>
<td>Pt 0.5</td>
<td>Nafton 212</td>
<td>(Pt/TiO₂)-(Ir/TiO₂) 1mg/cm²</td>
<td>Stable for 9 cycles at 0.7V in FC mode and 1.5V in EC mode (36hrs)</td>
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<td></td>
<td>mg/cm²</td>
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<td>mg/cm² 1</td>
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<td></td>
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<td>mg/cm² 1</td>
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</tr>
<tr>
<td>Jung et al. [67]</td>
<td>Pt/C 0.5</td>
<td>Nafton 112</td>
<td>Pt-Ir (85wt. % Pt) 4mg/cm²</td>
<td>5 times lower degradation rate than URFC with carbon-based BPPs</td>
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<td></td>
<td>mg/cm²</td>
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<td>mg/cm² 4</td>
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<td></td>
<td>mg/cm² 4</td>
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</tr>
<tr>
<td>Jung et al. [68]</td>
<td>Pt 0.5</td>
<td>Nafton 112</td>
<td>Pt-Ir (85wt. % Pt) 4mg/cm²</td>
<td>Stable for 4 cycles at 300mAcms⁻² (100hrs)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>mg/cm²</td>
<td></td>
<td>mg/cm² 4</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>mg/cm² 4</td>
<td></td>
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</tr>
</tbody>
</table>

Note: Estimated value from the figure in the literature; For the composite BOCs, “A-B” means mixed A and B, while “A/B” means A supported on B
### Table-3 Suitable catalyst supports for BOCs reported in the literature

<table>
<thead>
<tr>
<th>References</th>
<th>Catalyst support</th>
<th>Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chen et al. [37, 38]</td>
<td>Ti$<em>{0.9}$Nb$</em>{0.1}$O$_2$</td>
<td>Quite good stability against electrochemical oxidation due to its non-defective oxygen lattice</td>
</tr>
<tr>
<td>Ganesan et al. [39]</td>
<td>Nb-doped TiO$_2$</td>
<td>Better stability than carbon support at more anodic potentials</td>
</tr>
<tr>
<td>Huang et al. [18, 36]</td>
<td>TiO$_2$</td>
<td>High fuel cell performance and ultrahigh stability at high potentials; Round-trip efficiency was improved by the catalyst support.</td>
</tr>
<tr>
<td>Sui et al. [40]</td>
<td>TiC</td>
<td>Pt-Ir/TiC catalyst prepared by the plasma process was more active than that by the chemical process.</td>
</tr>
<tr>
<td>García et al. [42]</td>
<td>TiC and TiCN</td>
<td>TiCN support showed better corrosion resistance than TiC support at anodic potentials.</td>
</tr>
<tr>
<td>Roca-Ayats et al. [43]</td>
<td>TiC, TiCN, and TiN</td>
<td>TiCN supported catalyst yielded the highest activity towards ORR &amp; OER in addition to the best compromise between catalytic activity and stability.</td>
</tr>
<tr>
<td>Fuentes et al. [41]</td>
<td>TiC</td>
<td>No short-term degradation; Round-trip efficiency as high as 65% was achieved at the lower kinetic current density region.</td>
</tr>
<tr>
<td>Pai et al. [44]</td>
<td>Graphitized carbon</td>
<td>Higher round-trip efficiency and better stability than carbon black catalyst support</td>
</tr>
<tr>
<td>Cruz et al. [45]</td>
<td>Sb-doped SnO$_2$ (ATO)</td>
<td>Stability was quite good for 400min FC operation at 0.6V and 400min EC operation at 1.55V.</td>
</tr>
</tbody>
</table>

### Table-4 Suitable GDLs for UR-PEMFCs reported in the literature

<table>
<thead>
<tr>
<th>Reference</th>
<th>GDL</th>
<th>Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ioroi et al. [56]</td>
<td>Ti fiber</td>
<td>A stable operation can be achieved with the appropriate PTFE loading on the Ti GDB.</td>
</tr>
<tr>
<td>Wittstadt et al. [53]</td>
<td>Ti foam</td>
<td>PTFE coating on the Ti foam led to better stability than the untreated Ti foam.</td>
</tr>
<tr>
<td>Ito et al. [57]</td>
<td>Ti felt</td>
<td>Larger fiber diameter of Ti felt harms the EC performance but improves the FC performance.</td>
</tr>
<tr>
<td>Ito et al. [60]</td>
<td>Ti felt</td>
<td>MPL has little effect on the EC performance, but can significantly improve the FC performance under fully humidification condition.</td>
</tr>
<tr>
<td>Hwang et al. [58]</td>
<td>Ti felt</td>
<td>The highest round-trip efficiency was achieved by the Ti felt GDB with large fiber diameter (80µm) under a temperature of 80℃.</td>
</tr>
<tr>
<td>Hwang et al. [61]</td>
<td>Ti felt</td>
<td>MPL has little effect on the EC operation, but can significantly improve FC performance under fully humidified condition.</td>
</tr>
<tr>
<td>Song et al. [65]</td>
<td>Carbon paper</td>
<td>FC performance was as good as the conventional carbon-based GDL, but EC performance was much higher; The cycle stability was improved for over 20 cycles.</td>
</tr>
<tr>
<td>Chen et al. [62]</td>
<td>Carbon paper</td>
<td>Similar initial performance with the conventional GDL with carbon black MPL, but achieved much better stability during the cycle test for over 60 hrs.</td>
</tr>
<tr>
<td>Huang et al. [66]</td>
<td>Carbon paper</td>
<td>Much better stability in the cycle test for 36hrs.</td>
</tr>
<tr>
<td>Jung et al. [16]</td>
<td>Carbon paper</td>
<td>Similar FC and EC performance with conventional GDL, but with much better stability.</td>
</tr>
<tr>
<td>References</td>
<td>BPPs</td>
<td>Performance</td>
</tr>
<tr>
<td>--------------------</td>
<td>-------------------------------------------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Jung et al. [67]</td>
<td>Au-coated Ti BPPs</td>
<td>Five times lower voltage degradation rate than the carbon-based BPPs.</td>
</tr>
<tr>
<td>Jung et al. [68]</td>
<td>Pt-coated Ti BPPs</td>
<td>Improved FC and EC performance compared with bare Ti-BPPs; Cycling stability was also very good for more than 100 hrs.</td>
</tr>
<tr>
<td>Zhang et al. [69]</td>
<td>Ti-Ag film coated on Ti BPPs</td>
<td>Interfacial contact resistance was much smaller than the bared Ti BPPs; Anti-corrosion ability was also improved; Better water management was achieved due to the low surface energy.</td>
</tr>
<tr>
<td>Zhang et al. [71]</td>
<td>Honeycomb-like nanocomposite Ti-Ag-N film coated on Ti BPPs</td>
<td>Superior conductivity attributed to the evenly embedded Ag nanoparticles in Ti$_2$N matrix; Great corrosion-resistance was also achieved.</td>
</tr>
<tr>
<td>Lin et al. [72]</td>
<td>(Ti,Zr)N-coated Ti BPPs</td>
<td>Corrosion resistance was improved by 200 times.</td>
</tr>
<tr>
<td></td>
<td>(Ti,Zr)N-coated stainless steel BPPs</td>
<td>Corrosion resistance was improved by 215 times.</td>
</tr>
<tr>
<td>References</td>
<td>Stack features</td>
<td>Single cell features</td>
</tr>
<tr>
<td>------------------</td>
<td>-----------------------------------------------------</td>
<td>-----------------------------------------------------------</td>
</tr>
<tr>
<td>Su et al. [83]</td>
<td>6 cells in series; Shared membrane; Hydrogen storage alloy</td>
<td>Pt/C (40 wt.%) 0.4mg/cm²; Nafion 112; Pt-IrO₂ (60:40 wt. ratio) 0.7mg/cm²</td>
</tr>
<tr>
<td>Sone et al. [79]</td>
<td>17 cells in series; Closed system</td>
<td>Pt-IrOₓ</td>
</tr>
<tr>
<td>Grigoriev et al. [80]</td>
<td>7 cells in series; Reduction and oxidation electrodes;</td>
<td>Pt/C (HER&amp;ORR) 0.8mg/cm²; Nafion 1135; Pt-Ir (1:1 wt. ratio, HOR&amp;OER) 1mg/cm²</td>
</tr>
<tr>
<td>Millet et al. [81]</td>
<td>2 cells; Reduction and oxidation electrodes;</td>
<td>Pt/C (HER&amp;ORR) 0.8mg/cm²; Pt-Ir (1:1 wt. ratio, HOR&amp;OER) 1mg/cm²</td>
</tr>
</tbody>
</table>

**Table-6** UR-PEMFC stack development reported in the literature
Fig. 1 Comparison between RFC and URFC: (a) RFC; (b) URFC.

Fig. 2 Schematic diagram of various URFC technologies operated in FC and EC modes: (a) UR-PEMFC; (b) UR-AFC; (c) UR-SOFC with oxygen ion conducting electrolyte; (d) UR-SOFC with proton conducting electrolyte.
Fig. 3 Composition of a typical UR-FEMFC single cell: (a) main cell components; (b) TEM micrograph of Pt supported on carbon [77]; (c) catalyst layer deposited on PEM [47]; (d) Carbon paper GDL [58]; (e) Commercial BPPs (from http://www.mgm-carbon.com/products/carbongraphitefelt/9.html)

Fig. 4 Various structures of the deposited Pt-IrO₂ composite BOCs: (a) IrO₂ deposited on Pt [31]; (b) Pt deposited on IrO₂ first and then mixed with Pt [19]; (c) Pt supported on Ir-deposited IrO₂ [33]; (d) Pt supported on IrO₂ [30]; (e) RuO₂ and IrO₂ supported on Pt [15]; (f) Ir@Pt nanodendrites [32]
**Fig. 5** Various catalyst layer structures on the oxygen side [55]: (a) one-layer composite electrode; (b) multilayered electrode; (c) segmented electrode. (“FC” stands for fuel cell catalyst, i.e. Pt; “EC” stands for electrolysis cell catalyst, i.e. IrO$_2$)

**Fig. 6** GDL in UR-PEMFCs: (a) schematic diagram of the GDL structure; (b) Ti-felt GDB [61]; (c) Ti-felt GDB coated with Ti-powder MPL [61].
Fig. 7 Stability of UR-PEMFC performance after running cell at 2.0V for 1 h every day [68], with: (a) carbon-based BPPs; (b) Pt-deposited Ti-BPPs.

Fig. 8 Different flow channels of the BPPs on the oxygen side [70]: (a) serpentine-single channel; (b) serpentine-double channel; (c) parallel channel.
Fig. 9 Two different electrode configurations for UR-PEMFCs: (a) hydrogen and oxygen electrode configuration; (b) reduction and oxidation electrode configuration.

Fig. 10 UR-PEMFC stacks reported in the literature: (a) in-lab stacks by Sone [79], Grigoriev et al. [80], and Millet et al. [81] (From left to right); (b) Commercial stacks by Proton Inc. [11], LLNL [11], and Lynntech, Inc. [78] (From left to right).
Fig. 11 UR-PEMFC systems: (a) a schematic model [84]; (b) a practical model [79]

Fig. 12 Schematic representation of UR-PMFC applications in various fields (Figures of renewable energy, electric grid, laptop and cellphone from: http://all-free-download.com; Figures of space shuttle, satellite, airplane, cars, and UPS from http://openclipart.org)