Investigation of the open bifunctional cathode for unitized reversible fuel cell: composition and performance

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Abstract. Unitized regenerative fuel cell (URFC) can operate both in energy generation (EG) and in hydrogen production (HP). Using URFC reduces the weight and size characteristics of the power plant compared to a stationary system with the independent fuel cell and the electrolyzer. However, its performance also reduces. In this work, we study URFC with an open cathode, which applied as the anode in HP. In this case, the air inflow to the FC cathode in EG, and oxygen outflow from the anode into the environment in HP. The investigation of the electrocatalysts composition for the bifunctional cathode is carried out. The advantages of using a mixture of Pt40/RGO (RGO – reduced graphene oxide) with Ir-black (3:1) for an open cathode of URFC are shown. The cathode composition presented above doubles the efficiency of URFC in comparison with URFC based on a mixture of Pt-black and Ir-black (2:1).

1. Introduction

URFC with a proton exchange membrane (PEM) combines a fuel cell for EG and an electrolyzer for HP [1]. The above technological solution reduces the mass-size of the energy power plant and lowers its cost. However, it increases the technical complexity of the electrochemical system [2]. Significant importance is given to improve the stability and the efficiency of the catalytic layers in both URFC modes [3,4], which determines the performance and lifetime of the device.

A stable and highly active bifunctional oxygen catalyst, as is known, is one of the critical problems for the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) on the URFC air electrode (cathode). Nowadays, the absence of an optimal bifunctional electrocatalyst is the main barrier to the introduction of URFC as an effective electrochemical device. The performance of the URFC depends on the reversibility of the electrode reaction, which is closely related to the activity of bifunctional catalysts [5]. Regarding bifunctional catalysts, the use of various supports is critical to ensure a high surface area and dispersion of catalytic particles. Different bifunctional catalysts based on multiple carriers (carbon, modified carbon, and non-carbon carriers) are studied [6].

Platinum is the long-using and still the most efficient and stable bifunctional hydrogen catalyst for URFC [7]. Great efforts were to reduce the electrocatalyst loading to 0.5 mg/cm², given the deficit and high cost of Pt.

The cathode catalytic layers (CL) participate in the reaction of reduction and oxygen evolution. These catalysts should have high catalytic activity, long-term stability, high electronic conductivity, and low cost. Currently, the selection of cathode catalysts for URFC is still limited to noble metal catalysts.
Various research works were carried out, including the optimization of both composition and the support of the catalyst [8].

Today, most cathode electrocatalysts used in URFC are still noble metals based on a combination of platinum (Pt), ruthenium (Ru), iridium (Ir), and their oxides. Pt is the preferred catalyst for the ORR, but not suitable for the OER. In contrast, preferred catalysts for the OER, such as Ru, Ir, and their oxides, are not suitable for ORR. Therefore, a compromise is achieved by combining Pt with Ru, Ir, or their oxides in a composite electrocatalytic layer.

The authors of [9] found that the Pt-Ir double interaction region is highly active, both ORR and OER with improved corrosion resistance. However, the activity and stability of a mixture of Pt-Ru-Ir were slightly lower than Pt-Ir. Ru and its oxides turn out to be unstable under operating conditions of URFC [10]. Thus, the combination of Pt and Ir or its oxides is currently the leading choice of a cathode electrocatalyst. Now, various studies are being carried out on their elemental ratio, the method of preparation of the catalyst, microstructure, etc.

From [11], it follows that there is no specific optimal ratio between Pt-black and Ir-black, of which the proportion of Ir (or IrO₂) can vary from 1 wt. % to 50 wt. % in various studies. This discrepancy may be due to various methods of preparation of the catalyst/electrode. In general, the proportion of Pt-black should be more than half, due to the inability of Ir to participate in the oxygen reduction reaction. In addition to the direct mixing of the catalysts, various synthesis methods have been developed, including Pt supported on IrOₓ and IrOₓ supported on Pt [12]. Electrocatalysts obtained by these methods have better characteristics vs the Pt-black and Ir-black mechanic mixture.

The catalyst carrier plays an important role in the operation of the URFC. Vulcan XC-72 carbon black is used as a carrier in a standard FC with PEM. Due to the high anodic potentiodynamic polarization, this carrier is not suitable for URFC [13]. The titanium oxides, titanium carbides, and graphitized carbon are investigated as proposed carriers.

For a cathode in an FC with PEM, hydrophobized carbon paper or carbon cloth is used as gas diffusion electrodes (GDE) [14]. The gas diffusion base, which is pure carbon paper or cloth, is usually one-side coated with a hydrophobic microporous layer (MPL). The primary function of the MPL is to remove water from the active sites of the catalytic layer. A thin titanium plate of titanium powder usually used as an electrode for an electrolyzer [15]. The performance of the URFC battery in both hydrogen production and energy generation requires GDE optimization to provide high efficiency of inflow and outflow of the gases.

It is important to control the water balance in the catalytic layer. On the one hand, an FC operation needs hydrophobic support of CL to prevent flooding of the active sites. On the other hand, the electrolyzer operation needs hydrophilic support of CL. This issue implies a delicate balance between the content of the hydrophobized carbon support and the hydrophilic ionomer into the electrocatalyst layer, especially for the cathode electrode [16].

The aim of our research work was to determine the composition and performance of the bifunctional cathode URFC. We studied the effects of various compositions and GDE on the performance of the MEAs in EG and in HP.

2. Materials and methods

2.1. Electrocatalyst synthesis
A reduced graphene oxide (RGO) was used as the support. RGO synthesis was described in [17]. The synthesis of Pt₄₀/RGO (40 wt.% of Pt), Pt black, and Ir black catalysts were carried out by a chemical reduction method using ethylene glycol as described in [18].

2.2. Structural studies
We studied electrocatalysts on a scanning/transmission electron microscope (S/TEM) Titan™ 80-300 S/TEM (Thermo-Fisher Scientific, Beverly, MA, USA) (80-300 kV).

2.3. Electrochemical studies
Cyclic voltammograms (CVs) were recorded using potentiostat Solartron 1285 (AMETEK, Inc., Berwyn, PA, USA) at 25 ± 2 °C with a sweep rate of 20 mV/s in a deaerated 0.5 M H₂SO₄ solution saturated with N₂ at atmospheric pressure. The reference electrode was Ag\AgCl\KCl saturate, and the counter electrode was Pt-wire.

2.4. Electrodes and MEAs preparation
The electrocatalytic layer was placed directly to the Nafion® 212 membrane. The pre-prepared membrane in H⁺-form was fixed using a vacuum. Catalytic ink, which is a mixture of a catalyst and an ionomer in a water-alcohol solvent, was sprayed to the membrane using an airbrush. The membrane-electrode assemblies (MEAs) consisted of anodic and cathodic gas diffusion layers (GDLs) and a polymer ion-exchange membrane with deposited CL. We used the ELAT® 1400 LT brand with a one-side MPL as the GDL. We also used hydrophilic carbon cloth («RC», Russian) without a MPL. We used a URFC with an open cathode, which applied as the anode in HP. The area of the electrodes is 7 cm².

2.5. The electrochemically performances

2.5.1. Energy generation (EG). The i-V curves were recorded using the Solartron 1285 (AMETEK, Inc., Berwyn, PA, USA) potentiostat in the potential range from 0.9 to 0.1 V in the potentiodynamic mode with a sweep rate of 0.2 mV/s. Registration in the potentiodynamic mode was carried out at 0.5 V for 2 hours. The operating temperature of the cell is 35 °C. The URFC was fed by dry hydrogen to the anode and atmospheric air to the open cathode using a compressor without humidity control.

2.5.2. Hydrogen production (HP). The i-V curves were recorded using an automated current source and a multimeter at 60 °C and 80 °C. First, the URFC in HP worked in the potentiostatic mode at 1.5 V, and then the i-V curves were recorded.

URFC tests were also carried out by cycling the operating modes to determine the durability of its operation. The water supply to HP takes place in the anode.

Switch-over between URFC modes was carried out after 1 hour of stable operation of the device. The i-V curves were removed immediately before the regime change. The total number of cycles was 30.

3. Results and discussion.

3.1. Results of structural studies
Figure 1 shows TEM images of CL used for the open cathode of the URFC.

For the Pt40/RGO electrocatalyst, the average individual Pt-particles size was about 3.3 nm. As can be seen, platinum particles uniform distributed the surface of the carrier (figure 1a, b). Figure 1c shows the catalytic layer placed on the membrane with a loading of the catalysts equal to 1 mg/cm² and an ionomer content of 22 wt.%. The thickness of the supported catalyst layer is close to the thickness of the membrane and equal to 40-45 μm.

Figure 2 shows a SEM image of a mechanical mixture of Pt-black and Ir-black particles (PtIr) in a 2:1 ratio deposited on an MPL of the GDL (ELAT® 1400 LT carbon cloth) and pure carbon cloth RC (Russia). The average size of particles of a PtIr (2:1) was about 6.5 nm. It is noted the high uniform distributed of the deposited layer and the absence of significant agglomeration of particles.

3.2. Results of electrochemical studies
The catalyst’s electrochemically active surface area (EASA) was calculated using the hydrogen adsorption-desorption peaks at −0.15 - −0.2 V vs. Ag/AgCl (sat.) as described in [17]. EASA for the Pt40/RGO sample was 48 m²/g, for the Pt-black was 18 m²/g. On both curves, pronounced peaks are observed in the region of hydrogen desorption, corresponding to reflections from the face-centred cubic lattice (FCC) of platinum Pt (111) and Pt (200) (figure 3a). The surface of the carbon-supported catalyst is higher due to the smaller particle size and their more dispersion.
The shape of the CV curve for Ir black (figure 3b) is characterized by the presence of several broad peaks at potentials > 0.4 V, corresponding to redox transitions in the solid-state that occur due to the adsorption and oxidation of oxygenated particles from the electrolyte.

Figure 1. TEM image of Pt40/RGO (a, scale bar 5 nm) and particle size distribution (b), as well as the CL on the membrane (c, scale bar 50 μm, ionomer content 22 wt.%).

Figure 2. SEM images of a mechanical mixture in ratio 2:1 of Pt-black and Ir-black (a, scale bar 100 nm) with particle size distribution (b) and pure carbon cloth RC (c, scale bar 300 nm).

Figure 3. CVs for Pt40/RGO and Pt-black (a) and for Ir-black (b) catalysts recorded in 0.5 M H₂SO₄ solution at 25 ± 2 °C, and a sweep rate of 20 mV/s.
3.3. Testing MEAs of URFC

3.3.1. Energy generation. Figure 4 shows the i-V and power curves of the MEAs with different catalysts composition on the open cathode. The presence of Ir-black did not significantly affect the performance of URFC in EG, regardless of the composition of the catalytic mixture on the cathode and the GDL used (red and green lines in figure 4).

The MEA in which a mixture of Pt40/RGO and Ir-black was used in a ratio of 3:1, GDL – ELAT® 1400 LT, the current density at an operating mode of 0.5 V is 0.28 A/cm². This performance was the maximum among all studied MEAs. The result in the case of using a similar cathode, but hydrophilic GDL – «RC» was inferior to the previous one and was 0.22 A/cm². This due to difficulties in the removal of water from active sites of the catalyst and partial flooding of the CL.

![Figure 4. i-V and power curves for MEAs URFC in EG with various catalysts on the cathode (red lines - Pt40/RGO, green lines - a mechanical mixture of Pt40/RGO and Ir-black (Pt40/RGO-Ir) in the ratio 3:1, black lines - a mechanical mixture of Pt-black and Ir-black in a ratio of 2:1) and GDEs (solid line – ELAT® 1400, dotted line - hydrophilic cloth «RC»): 1 – Pt40/RGO, GDE - ELAT; 2 - Pt40/RGO, GDE – «RC»; 3 - PtIr (2:1), GDE - ELAT; 4 PtIr (2:1), GDE – «RC»; 5 - Pt40/RGO-Ir (3:1), GDE - ELAT; 6 - Pt40/RGO-Ir (3:1), GDE – «RC». The catalysts loading equal to 2 mg/cm². Anode catalyst was Pt40/C10 (= 40 wt.% of platinum on Vulcan XC-72 with 10 wt. % of PTFE). The loading of the catalyst was 1 mg/cm². Membrane was Nafion 212.](image)

A significantly lower performance was obtained for the MEA, which used a PtIr (2:1). In the case of hydrophobic GDL, this is due to the low performance of the CL, which reduces the rate of electrochemical processes. Another reason was the low EASA of the Pt-based catalyst compared to Pt40/RGO. A significant drop in efficiency when using a PtIr mixture and hydrophilic GDE is explained by the formation of a film of liquid water which flooding the active sites in the volume of the CL.

The use of an open cathode causes additional difficulties in feeding reagents to the CL of the cathode, which reduces the overall performance of URFC in EG. At the same time, the MEAs water balance management under conditions of feed of dry reagents causes considerable difficulties. As shown in figure 5 hydrophilic GDL allowed improving the quality of water balance control in URFC and maintaining high current density values (voltage 500 mV) for 30 minutes compared to 10 minutes for hydrophobic GDL. Note that both electrodes were carbon cloth of similar thickness and structure.

3.3.2. Hydrogen production. In HP, the open cathode of URFC operate as the anode of the electrolyzer. We noted that the supply of water in HP was carried out in the cathode of the electrolyzer. Due to the high anodic potentiodynamic polarization, the air electrode should have the highest degradation stability. Therefore, a mechanical mixture of Pt-black and Ir-black was most often used as a bifunctional CL [18]. However, due to the low performance of the catalytic layer in EG, CL based on a mechanical mixture of Pt40/RGO and Ir-black was also studied. The result obtained is shown in figure 6.

The use of hydrophobic GDL reduced the performance of URFC regardless of the structure of the electrocatalytic layer (figure 6) since the determining factor was the low rate of water supply to the cathode through the membrane. Performance of URFC, in this case, determined by the water feed rate.
In turn, the MEA URFC with a bifunctional cathode based on a mechanical mixture of Pt40/RGO and Ir-black in a ratio of 3:1 was not inferior in performance to a cathode based on a mechanical mixture of Pt-black and Ir-black in a 2:1 rate and even surpassed the latter (figure 6).

![Image](image_url)

**Figure 5.** Potentiostatic curves at a voltage of 500 mV for MEAs 5 - a mechanical mixture of Pt40/RGO and Ir-black in a ratio of 3:1, GDL - ELAT and 6 - a mechanical mixture of Pt40/RGO and Ir-black in a ratio of 3:1, GDL - «RC». The catalysts loading equal to 2 mg/cm². Anode catalyst was Pt40/C10. The loading of the catalyst was 1 mg/cm². Membrane was Nafion 212.

The data obtained are showed that the advantages of using a mechanical mixture of Pt40/RGO and Ir-black in a 3:1 ratio as a bifunctional open cathode of URFC are deposited on a membrane in combination with GDÉ based on hydrophilic cloth. This result is determined by the low performance of the used CL in EG and the need to supply water through the anode. URFC showed the stability of the obtained characteristics during 30 cycles during the changing of modes. The improved durability of the Pt/RGO catalyst was related to the structure and properties of the RGO-carrier and was described in detail in the [17].

4. **Conclusions**
In the present work, we studied URFC with an open cathode FC, which acts as the anode of the electrolyzer. Air is supplied to FC cathode, and oxygen in the electrolyzer is released into the environment. The study and optimization of the composition of the electrocatalytic layer of the bifunctional cathode was carried out. The advantages of using a mixture of Pt40/RGO and Ir-black as a cathode of URFC of this design were shown in comparison with a mixture of Pt-black and Ir-black both in terms of performance (2 times higher). It was concluded that the advantages of using a mechanical mixture of Pt40/RGO and Ir-black in a ratio of 3:1 as a bifunctional open cathode of URFC are applied to the membrane in combination with GDE based on hydrophilic cloth. This result is determined using RGO as catalytic support in the cathode CL and the need to supply water through the anode. URFC showed stability of the obtained indicators during 30 cycles of switching modes.
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