FUEL CELLS BASED ON SOME PROTON DYNAMICS PROPERTIES OF H_2O_2 COMPOUND

M. Davidović[1,], S. Linić[1], A. Janićijević[2], Z. Nedić[3] and U. Mioč[3]*

[1,*] Institute „Gosa" Belgrade, Milana Rakića 35, Serbia
[2] University of Belgrade, Faculty of Technology and Metallurgy, Belgrade,
Karnegijeva 4, Serbia
[3] University of Belgrade, Faculty of Physical Chemistry, Belgrade,
Studentski trg 12-16, Serbia

Abstract: Electrochemical and conductive performances of the H_2O_2 compound in function of ambient conditions have been studied. A number of experimental techniques and theoretical calculations have been applied also to this problem. Namely, hydrogen peroxide with molecular formula (H_2O_2) compound obtained from polyoxometalates acids which have small specific surface (5 m^2/g), will be the main subject of this study. The mentioned characteristics can be improved by plating particular conductors on transparent substrate in order to improve their properties.

Keywords: fuel cell, hydrogen peroxide, space charge region.

1. INTRODUCTION

Hydrogen peroxide is a very blue liquid, slightly more viscous than water, that appears colorless in dilute solution. It has strong oxidizing properties.
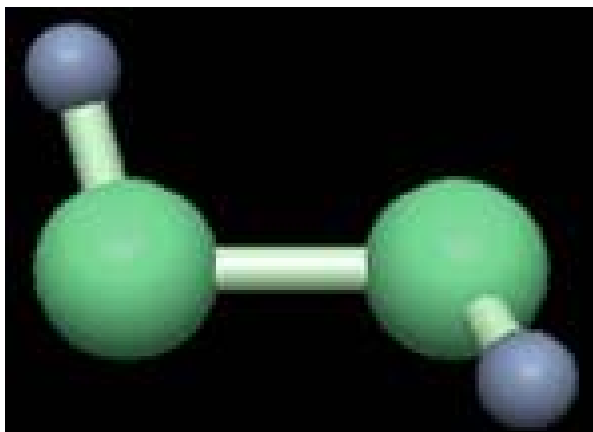

Figure 1.

By using proper electrocatalysts, H_2O_2 can be converted into hydroxyl radicals OH, as shown in Fig. 1. Also hydrogen peroxide adopts a nonplanar structure of C_2 symmetry. The properties of aqueous solutions of hydrogen differ from those of the neat material, reflecting the effects of hydrogen bonding between water and hydrogen peroxide molecules. Hydrogen peroxide and water form a eutectic mixture, exhibiting freezing–point depression (Fig.2).
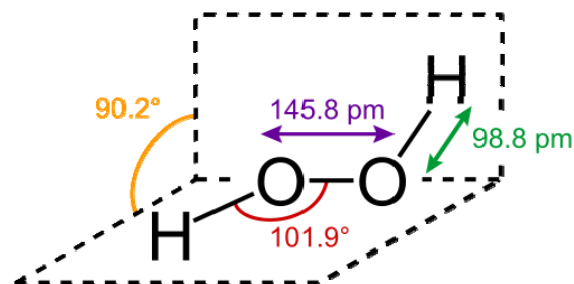

Figure 2.

The properties of hydrogen peroxide differ from those of neat material, reflecting the effects of hydrogen bonding between water and hydrogen peroxide molecules. Hydrogen peroxide decomposes exothermically into water and oxygen gas spontaneously, shown in Fig.3. and expressed by (1) [1,2].

$$2\ H_2O_2 \rightarrow 2H_2O + O_2 \qquad (1)$$

This process is thermodynamically favorable. The rate of decomposition is dependent on the temperature and concentration of the peroxide as well as the pH.

This mechanism can be employed as a means of producing humidified oxygen gas at high temperatures, as required sometimes to achieve reasonable kinetics. The resulting system is limited in energy density due to lost heat, but advances in catalysis are lowering the necessary activation energy of both oxygen and hydrogen peroxide reduction to the point where ambient systems may soon operate at compa-

*Corresponding author: milorad.davidovic@gmail.com

rable power densities. The electrochemical decomposition [3] analoguous with a theoretical half-cell voltage of 0,87 V/SHE can be thought of as expressed in (2)

$$HO_2^- + H_2O + 2e^- \rightarrow 3OH^- \tag{2}$$
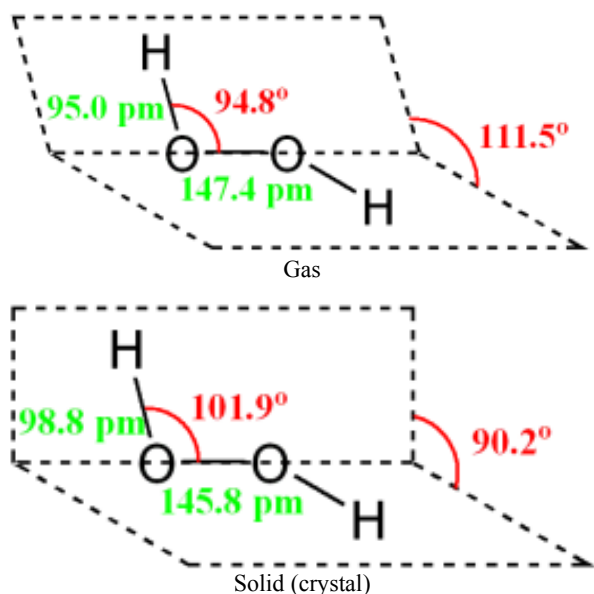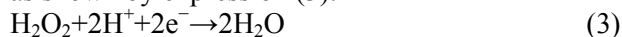

Gas

Solid (crystal)
Figure 3.

All potentials will be reported versus the standard hydrogen electrode (SHE). A second mechanism is the full reduction of the species to water, occurring at a theoretical half-cell potential of 1,87 V, as shown by expression (3).

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \tag{3}$$

Reduction of 100% hydrogen peroxide in a fuel cell utilizing (3), would give a volumetric energy density of 8,0 kWh/l.

As we know from previous study of different protonic species H^+, H_2O, H_3O^+, $H_5O_2^+$ similar dielectric behavior can be expected in this compound.

2. USE OF H₂O₂ AS A FUEL-ROCKET PROPELLENT

In this case, the H_2O_2 is typically passed over a catalyst, usually a silver mesh. The catalyst causes the oxygen and hydrogen in H_2O_2 to separate into O_2 and H_2 which then recombine explosively to form H_2O (water).

3. NaBH₄ AS A FUEL FOR THE FUEL CELL

The use of aqueous solution of NaBH₄ as a hydrogen carrying medium is relatively a new development. Combined with liquid hydrogen peroxide in a fuel cell (FC), shown by Fig. 4. and Fig.5, it brings some new advantages merits including [4], [5]:

−   Compact and convenient all-liquid operation;
−   Built-in supercapacitor effect as the carbon particles of the electrode and the all liquid anolyte/catholyte form a solid-liquid double layer giving excellent short-time overload capability;
−   Unitized regeneration is enabled since the catalytic electrodes and the membrane electrolyte only need to be hydrophilic, unlike ordinary H_2O_2 FC where both hydrophilic and hydrophobic phases are required to maintain a fragile three phase (gas-liquid solid) interface;
−   Storage of the regenerated reactants in the NaBH₄/H₂O₂ FC is straight-forward
−   Fast discharge/recharge is obtained through the fast dynamics of H^+ and OH^- ions in a water-based solution
−   Fast/deep charge/discharge is of paramount importance for Low Earth Orbit (LEO) applications, effectively translated into a high LEO cycle energy density.

Tuning of the restarted GMRES method, which then typically converges after 20 to 25 iterations.

The half-cell reaction scheme for a cathode based on hydrogen peroxide in acidic media includes a combination of direct hydrogen peroxide reduction and indirect oxygen reduction following decomposition. The reactions and associated standard [6] potentials at 298 K are as shown in expressions (4), (5) and (6).
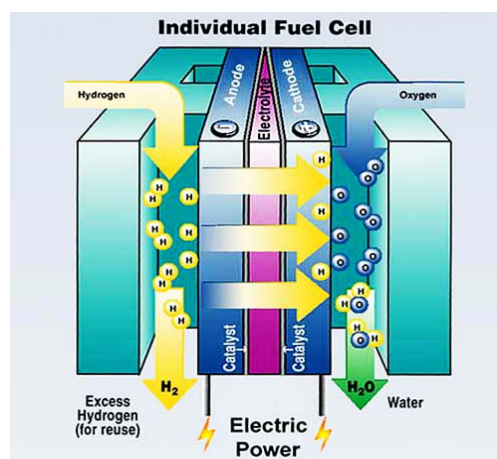
$$H_2O_2 + 2H^+ + 2e^- \leftrightarrows 2H_2O$$
$$E° = 1.776 \text{ V vs SHE} \tag{4}$$

$$H_2O_2 \leftrightarrows O_2 + 2H^+ + 2e^-$$
$$E° = 0.682 \text{ V vs SHE} \tag{5}$$

$$O_2 + 4H^+ + 4e^- \leftrightarrows 2H_2O$$
$$E° = 1.229 \text{ V vs SHE} \tag{6}$$

Figure 4.

Figure 5.

Figure 6. (Color online) Image of a micro fluidic fuel cell with Pd electrodes using formic acid (HCOOH) fuel and hydrogen peroxide (H₂O₂) oxidant. The cross-section overview of the channel shows the inter-diffusion of anolyte and catholyte that is characteristic of co-laminar flow. The channels employed here were 2 mm wide and 70–170 μm high, and the electrodes were 0.5 mm wide and 10 mm in active length.
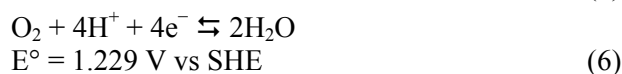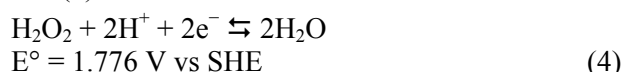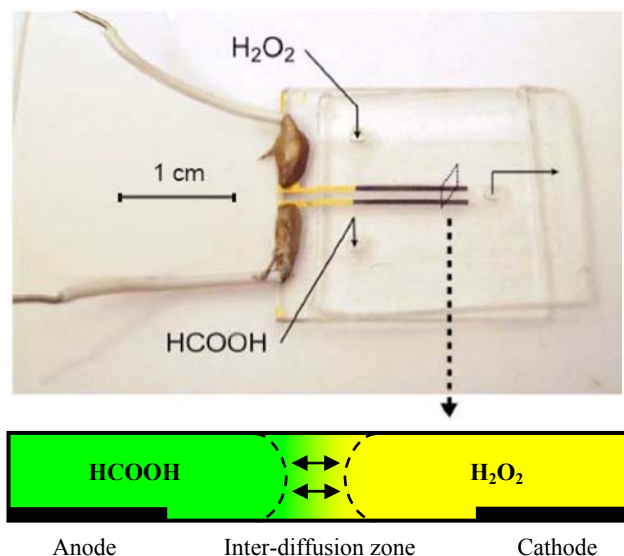
The standard potential for direct hydrogen peroxide reduction, reaction 1 expressed as in (4), is more positive than most other oxidizers e.g., oxygen or permanganate, therefore potentially establishing a higher electromotive force for fuel cell operation. However, the oxidation of peroxide to oxygen, reaction 2 expressed as in (5), is easy on both Pt and Pd, and both reactions 1 and 2 occur together, as expressed in (6). The effect of this is that the open circuit potential is a mixed potential, occurring at about 0,85 V on Pt in acid solution.

Net reduction of hydrogen peroxide occurs only negative of this, so the actual over potential for direct hydrogen peroxide reduction is relatively high. The combination of the two reactions is the catalyzed decomposition of hydrogen peroxide to oxygen and water, $2H_2O_2 \rightarrow 2H_2O + O_2$.

Anodic systems based on formic acid have previously exhibited relatively high performance in terms of both current density and power density in micro fluidic fuel cells [7] as well as polymer electrolyte membrane fuel cells based on liquid fuels, such as the direct formic acid fuel cell [8].

The half-cell reaction and standard potential at 298 K of a formic acid-based anode is expressed in (7).

$$CO_2 + 2H^+ + 2e^- \leftrightarrows HCOOH$$
$$E° = -0.199 \text{ V vs. SHE} \tag{7}$$

A fuel cell based on hydrogen peroxide reduction and formic acid oxidation thus has a standard cell potential of 1,975 V.

The fuel cell shown in Fig. 6 comprises two layers: a substrate upon which electrodes are formed, and a polymeric top layer housing the channel structure.

All the methods applied for the characterization of salts in this study, presented in the article "Characterization of potassium salts of 12-tungstophosphoric acid", confirm that in the synthesis of neutral or acidic salts, the reaction of WPA in concrete experiment with K_2CO_3, causes precipitation of K_3WPA. In the case of formation of acidic potassium salt, a mixture of K_3WPA and unreacted WPA is obtained. The nature of this mixture depends on the number of replaced protons-oxonium ions by cations. In the case of KH_2WPA salt, a two-phase system of cubic crystals of WPA and mesoporous neutral K_3PWA salt is formed. If the number of counter ions is x≥2, unreacted acid is dispersed over the grains of neutral salt. The effects of the interfaces in these heterogeneous systems, such as acid potassium salts of WPA, are of particular importance because of the (i) extremely high interfacial proportions and (ii) size effects that can affect the local transport properties [11]. If grain boundaries are composed of space-charge layers, the carriers can exhibit completely different transport properties along the core and space-charge layers [12]. Formation of extra defects in the space-charge region as a consequence of interface processes has a significant effect on ionic conductivity.

The results obtained in [8] confirm that insoluble potassium salts of WPA could be good candidates for application as proton exchange electrolytes

in fuel cells due to their satisfactory proton conductivity between 7.2×10^{-5} and 1.4×10^{-4} S/cm. Also, their possible washing out from electrolyte or membrane is avoided in contrast to soluble WPA. Their conductivity at 80^0C and RH = 70% is $\sigma = 10\ 2$ S/cm measured at a frequency of 100 kHz. The acidic KH_2WPA salt showed the best characteristics for this purpose which is in accordance with conductivity measurements and FT-IR data.

Although the investigated salts have shown good chemical stability and satisfactory conductivity, their application as potential material for fuel cells needs further technical improvements. We belie-

ve that further significant mechanical and conductive improvements can be reached by incorporation of this class of compounds into inorganic substrates such as SiO_2, TiO_2 and Al_2O_3 or organic polymer such as polyaniline [13].

3. FUEL CELL APPLICATIONS

Application ranges of FC are given in Table 1 [9].

Table 1.

TYPICAL APPLICATIONS	Portable electronics equipment.			Cars, boats, and domestic CHP.		Distributed power generation, CHP, and buses.		
MAIN	ADVANTAGES			Higher energy		Density to batteries		
POWER (W)	1	10	100	1K	10K	100K	1M	10M
APPLICATION RANGE FOR FUEL CELL CLASS				ACF ↔			MCFC ↔	
				SCFC ↔				
		PEMFC ↔						
					PAFC ↔			

4. CONCLUSION

Heteropoly compounds have been widely studied in relation to their expressive conductive, catalytic, antiviral, photochromic and many other properties [10]. Among heteropoly compounds, 12-tungstophosphoric acid hydrates, $H_3PW_{12}O_{40} \cdot nH_2O$ (WPA·nH_2O, n = 29, 21, 14 and 6) having Keggin structure, characterized by strong acidity are classified into "superacids". Systematic investigations of heteropoly acids (HPAs) and their alkali and alkaline-earth salts, the aim in this study was to examine whether insoluble potassium salts of WPA could be used as proton exchange electrolytes (PEE) in fuel cells. An important step towards better understanding and applying of PEEs is the characterization of their thermal, structural and conductive properties.

5. ACKNOWLEDGMENTS

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ГОРИВЕ ЋЕЛИЈЕ НА ОСНОВУ НЕКИХ СВОЈСТАВА ПРОТОНСКЕ ДИНАМИКЕ H₂O₂ ЈЕДИЊЕЊА

Сажетак: У раду су представљена електрохемијска својства и својство проводљивости H₂O₂ јединьења у зависности од амбијенталних услова. Бројне експерименталне технике и теоријски прорачуни примењивани су на овај проблем. Посебна пажња посвећена је јединьењу хидроген-пероксид, молекуларне формуле (H₂O₂), који је добијен из полиооксометал киселине, мале специфичне површине (5 m²/g). Поменута својства се могу унапредити облагањем појединих проводника на транспарентном супстрату.

Кључне речи: горивне ћелије, водоник пероксид, простор наелектрисања.
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