FUEL CELLS BASED ON SOME PROTON DYNAMICS PROPERTIES OF H$_2$O$_2$ COMPOUND

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Abstract: Electrochemical and conductive performances of the H$_2$O$_2$ 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$_2$O$_2$) 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.

By using proper electrocatalysts, H$_2$O$_2$ 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 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).

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].

$$2 \text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$$  \hspace{1cm} (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-
rable power densities. The electrochemical decom-
position [3] analogous with a theoretical half-cell
voltage of 0.87 V/SHE can be thought of as expres-
sed in (2)
\[
\text{HO}_2^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 3\text{OH}^- \quad (2)
\]

Figure 3.

All potentials will be reported versus the stan-
dard hydrogen electrode (SHE). A second mecha-
nism 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).
\[
\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O} \quad (3)
\]

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
protomic species H^+, H_2O, H_3O^+, H_5O_2^+ similar die-
lectric behavior can be expected in this compound.

2. USE OF H_2O_2 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. NaBH_4 AS A FUEL FOR
THE FUEL CELL

The use of aqueous solution of NaBH_4 as a
hydrogen carrying medium is relatively a new deve-
lopment. Combined with liquid hydrogen peroxide
in a fuel cell (FC), shown by Fig. 4. and Fig.5, it bri-
gs some new advantages merits including [4], [5]:
- Compact and convenient all-liquid operation;
- Built-in supercapacitor effect as the carbon par-
ticles 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 ca-
talytic electrodes and the membrane electrolyte
only need to be hydrophilic, unlike ordinary H_2O_2
FC where both hydrophilic and hydrophobic pha-
ses are required to maintain a fragile three phase
(gas-liquid-solid) interface;
- Storage of the regenerated reactants in the
NaBH_4/H_2O_2 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 im-
portance 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 iterati-
ions.

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 decomposi-
tion. The reactions and associated standard [6] po-
tentials at 298 K are as shown in expressions (4), (5)
and (6).

\[
\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{H}_2\text{O} \quad E^\circ = 1.776 \text{ V vs SHE} \quad (4)
\]
\[
\text{H}_2\text{O}_2 \rightleftharpoons \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \quad E^\circ = 0.682 \text{ V vs SHE} \quad (5)
\]
\[
\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O} \quad E^\circ = 1.229 \text{ V vs SHE} \quad (6)
\]
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, $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$.

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).

$$\text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{HCOOH}$$

$$E^\circ = -0.199 \text{ V vs. SHE}$$

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$_2$CO$_3$ causes precipitation of K$_3$WPA. In the case of formation of acidic potassium salt, a mixture of K$_3$WPA 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$_2$WPA salt, a two-phase system of cubic crystals of WPA and mesoporous neutral K$_3$PWA salt is formed. If the number of counter ions is $x \geq 2$, 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 $7.2 \times 10^{-5}$ and $1.4 \times 10^{-4} \text{ S/cm}$. Also, their possible washing out from electrolyte or membrane is avoided in contrast to soluble WPA. Their conductivity at $80^\circ\text{C}$ and RH = 70% is $\sigma = 10 \text{ S/cm}$ measured at a frequency of 100 kHz. The acidic KH$_2$WPA 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 believe 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$_2$O$_3$ or organic polymer such as polyaniline [13].

3. FUEL CELL APPLICATIONS

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

<table>
<thead>
<tr>
<th>TYPICAL APPLICATIONS</th>
<th>Portable electronics equipment.</th>
<th>Cars, boats, and domestic CHP.</th>
<th>Distributed power generation, CHP, and buses.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAIN</td>
<td>ADVANTAGES</td>
<td>Higher energy</td>
<td>Density to batteries</td>
</tr>
<tr>
<td>POWER (W)</td>
<td>1</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>APPLICATION RANGE FOR FUEL CELL CLASS</td>
<td>ACF</td>
<td>SCFC</td>
<td>PEMFC</td>
</tr>
</tbody>
</table>

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$_3$PW$_{12}$O$_{40}$·nH$_2$O (WPA·nH$_2$O, n = 29, 21, 14 and 6) having Keggin structure, characterized by strong acidity are classified into “supercarids”. 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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6. REFERENCES


**Gorive ğelije na osnovu nekih svojstava protonске dinamike H2O2 jediњeњa**

**Сажетак:** У раду су представљена електрохемијска својства и својство проводилиности H2O2 једињења у зависности од амбијенталних услова. Броjне експерименталне технике и теориjsки прорачунi применивани су на оваj проблем. Посебна пажња посвећена је једињењу хидроген-пероксид, молекулярне формулe (H2O2), коj је добиjен из полиоксометал киселине, мале специфичне површине (5 m2/g). Помеjутa своjства се могу унапредити облагањем поjединих проводника на транспарентном супстрату.

**Кључне речи:** гориве ћелије, водоник пероксид, простor наелектрисања.