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UREA/ HYDROGEN PEROXIDE FUEL CELL

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Urea fuel cells (UFCs) could be an effective method for generation of energy from urea fertilizer or wastewater containing urea. The purpose of this study is to demonstrate that electricity can be generated directly from urea when considering hydrogen peroxide as oxidants. Two types of catalysts are taken into account for UFC: Pt/C and Ni/MWCNTs for anode while using Pt/C as cathode catalyst. Polarization curves and power densities are studied for a couple fuel -oxidant: urea solution- hydrogen peroxide. The maximum power densities for Pt/C-Pt/C are about 0.03mW/cm^2, respective 0.05 mW/cm^2 for Ni/MWCNTs-Pt/C. Both UFC have showed a maximum potential in open circuit around of 400mV, respective 250mV.

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1. Introduction

Urea fuel cells (UFCs) could be an effective method for generation of energy from urea fertilizer, urine and residual waste water. Urine excretion product of human / animal waste is an energy source, considering that an adult can produce up to 11 kg of urea per year- the energy equivalent of 18 kg liquid hydrogen [1]. The most common approach in urea decomposition is urea electrocatalytic oxidation using noble metal catalysts [2-3] or non-noble metals, such as nickel and nickel composites [4-5]. In this context, Lan Rong et al. have demonstrated that fuel cells based on alkaline membrane and non-noble catalysts, such as Ni, Ag, and MnO_2, using humidified air as oxidant, can generate electricity directly from urea or urine [6]. In the absence of atmosphere need other oxidants to process urea in useful by-product. In this respect is taken in account hydrogen peroxide as a potential oxidant. In an urea/O_2 fuel cell the open circuit potential (OCV) reaches to 1.146 V at room temperature, slightly lower than the value of 1.23V of a H_2/O_2 fuel cell (Table 1)

Table 1. Oxidation/ Reduction reactions in a urea/humidified O_2 fuel cell.

	Reactant	**Reaction**	**E_0 (V)**
Cathode	Humidified O_2	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	
Anode	Urea	$CO(NH_2)_2 + 6OH^- \rightarrow N_2 + CO_2 + 5H_2O + 6e^-$	
Total Reaction		$\mathbf{2CO(NH_2)_2 + 3O_2 \rightarrow 2N_2 + 2CO_2 + 4H_2O}$	**+1.146**

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There are applications for collecting and conversion waste containing urea in useful or nontoxic by products where the oxidants (O_2, air) missing: space missions, spacelab or missions on the planets. Possible other oxidants to make fuel cells useful could be hydrogen peroxide. Hydrogen peroxide fuel cells have emerged as a new research for space or underwater applications: fuel cells using Al anode [7-10]; H_2/H_2O_2 and $NaBH_4/H_2O_2$ fuel cells [11-13].

Hydrogen peroxide has some advantages over oxygen. Since oxygen mass density in gas phase is typically a thousand times lower than in liquid phase, peroxide fuel cells can generate a higher current density. Another limiting aspect in a proton exchange fuel cell (PEMFC) is the two phase process of the reactants and product mass transport [14-17]; water generated during cathode reaction can condensate and block gas diffusion layer pores, limiting reactant transport. The cathode oxygen reduction reaction ($\mathrm{O_2 + 4H^+ + 4e^- \rightarrow 2H_2O}$) implies the transfer of four electrons [18-19]. There is 220mV potential drop when operating near open circuit potential with Pt electrocatalyst, caused by sluggish O_2 reduction reaction kinetics and by anode competing processes such as Pt-oxide formation [20-22]. On the other hand, the H_2O_2 reduction reaction on the cathode side involves the transfer of two electrons, i.e., a much lower activation barrier [23].

Based on hydrogen peroxide promising perspective in fuel cell applications, it is proposed a novel approach in urea fuel cell, i.e., using hydrogen peroxide as reactant at the cathode side. Oxidation and reduction reactions of the reactants, as well as the total reaction are shown in Table 2. In this case, the theoretical OCV of a urea/ hydrogen peroxide fuel cell is 1.76 V at room temperature, 0.614V higher than in the case of urea/O_2 fuel cell.

Table 2. Oxidation/ Reduction reactions in a urea/hydrogen peroxide fuel cell.

	Reactant	**Reaction**	**E_0 (V)**
Cathode	Hydrogen peroxide	$\mathrm{H_2O_2 + 2e^- \rightarrow 2OH^-}$	
Anode	Urea	$\mathrm{CO(NH_2)_2 + 6OH^- \rightarrow N_2 + CO_2 + 5H_2O + 6e^-}$	
	Total Reaction	$\mathbf{CO(NH_2)_2 + 3H_2O_2 \rightarrow N_2 + CO_2 + 5H_2O}$	**+1.76**

The theoretical estimation of the specific weight energy for urea system / 20% hydrogen peroxide with the molar concentration of the urea solution is shown in Fig. *1*. The specific energy was calculated considering a theoretical open circuit voltage of 1.76V, a voltage efficiency of 100% and the oxidant concentration- 20%. Human urine is an aqueous solution with a water content of more than 95%, the rest being other compounds, in order of decreasing abundance: urea 9.3 g/l (corresponding to 0.15 mol/l), Chloride 1.87 g/l, Sodium 1.17 g/l, Potassium 0.750 g/l, creatinine 0.670 g/l and other dissolved ions, organic and inorganic compounds. On the other hand, a saturated aqueous solution of urea has a urea content of 107.9 g/100 ml water at 20°C, which is the molar concentration of approximately 9.9 mol/l. If for highly concentrated urea solutions, close to saturation, the theoretical specific energy reaches to 428Wh/kg. Thus, for a urea fuel solution of 1mol/l, the theoretical specific energy is 177Wh/kg, while for a concentration of 0.15 mol/l, the energy is about 40Wh/kg.

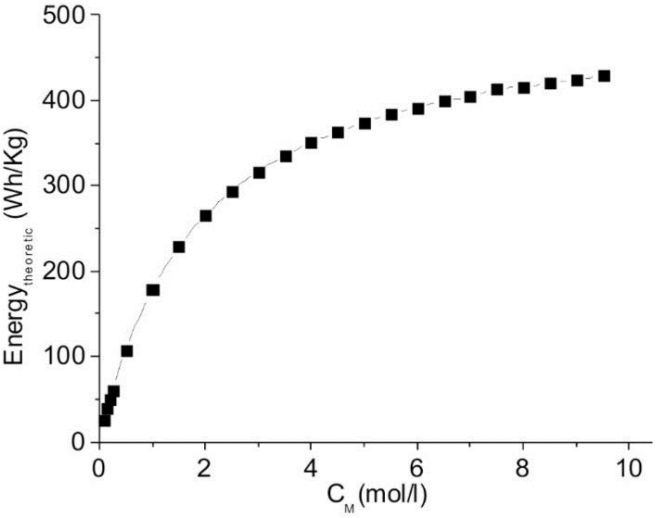

Fig. 1. Theoretical estimation of the specific energy dependency (considering the weight of reactants) of urea system / 20% hydrogen peroxide on the molar concentration of the urea solution

The purpose of this study is to demonstrate that electricity can be generated directly from urea when considering hydrogen peroxide as oxidant. Two different MEA configurations have been manufactured containing a proton exchange membrane and Pt/C or Ni/MWCNTs as anode catalysts, while Pt/C was used as cathode catalyst. Catalyst electrochemical behaviour in urea solution was tested using cyclic voltammetry and polarization curves were studied for a couple fuels -oxidant: urea solution- hydrogen peroxide. Gaseous products collected during experiments were analysed using a residual gas analyser, while the resulted anode solution was tested by means of mass spectrometry in order to determine its content.

2. Materials and methods

2.1 Materials

Membrane. Fumapem F1050- Conditioning: Fumapem F1050 in salt form was treated in 10% aqueous solution of HNO_3 for 3h at 90^0C. After washing with demineralized water the membranes were boiled in demineralized water for 1 h at 90^0C. Finally the membranes were washed with demineralized water (~pH 7) and stored in 0.5M H_2SO_4 solution.

Catalysts. Two types of catalysts were used: Pt/C (0.6-1 mg/cm^2 loading), respective Ni/MWCNTs (multiwall carbon nanotubes) (10 mg/cm^2 loading) for enhancing the active surface.

MEA: The Pt/C, respectively Ni/MWCNTs catalyst solutions were deposited onto carbonic micro porous substrate- carbon paper with an active surface of 9 cm^2 (3 cm x 3 cm). After conditioning, membranes with a 16 cm^2 (4 cm x 4 cm) surface were hot pressed (50kg/cm^2, 90^oC) against the catalyst loaded carbon papers to form MEA as described in

Table *3*.

2.2 Characterization methods

Catalyst electrochemical behaviour in urea solution was tested using cyclic voltammetry in a three electrode cell: reference electrode-Dynamic Hydrogen Electrode (DHE), auxiliary electrode- spectroscopic graphite bar and working electrode- catalyst deposited on a glassy carbon surface with a loading of 30 μg/cm^2. Two electrolyte solutions were used: 5.5M KOH and 0.33 M urea in 3.7 M KOH.

MEA testing. MEAs were tested in a fuel cell with two compartments for liquid feed. Peristaltic pumps (Wallace & Tiernam AAC 4342) were used for recirculating the anode (1M urea in 1.5M NaOH) and the cathode solution (20%wt. H_2O_2+5%wt. H_3PO_4), with flow rate of 100 ml/min. MEA-UFC polarization curve were obtained using an Agilent 6060B- controlled by LabVIEW interface.

Residual gas analysis. During experiments, it was observed the formation of gaseous products, which were collected using sterile vacuum containers and analysed using a residual gas analyser.

Mass spectrometry. Urea solutions were analysed after performing MEA testing for identifying the resulting products using a Schimadzu mass spectrometer with the following parameters: 2 LC-20AD Schimadzu pumps; 10 MPa maximum pressure; 30°C injector temperature; 0.2 ml/min flow rate of the mobile phase; eluent- Acetonitrile 99.8% (Sigma Aldrich); ionization techniques-ESI – electro pulverization; ESI potential – 1,5kV; CDL temperature (curve desolation line)- 250°C; 2.5kV interface potential.

3. Results and discussion

3.1 Catalyst: electrochemical evaluation

The two catalysts considered for urea oxidation, i.e. Pt/C and Ni/MWCNTs, were tested in relevant conditions for UFC operation using two electrolyte solutions: 5.5M KOH and 0.33 M urea in 3.7 M KOH (Fig. *2*). Figure 2 (1) shows a complex oxidation peaks on Ni/MWCNTs catalyst. There are two oxidation peaks one for Ni(0) in Ni(II) at ~270-300mV and second at ~900mV assigned to a molecular complex belong to Ni(III) region [24]. This molecular complex has a reduction potential at 600mV. Ni/MWCNTs electrochemical active surface (ESA) was estimated using the following relation: ESA = Q/(mq), where Q is the necessary charge for reducing the molecular complex (here associated with NiOOH to $Ni(OH)_2$ for simplified calculus) m- Ni catalyst mass on the electrode and q- the theoretical specific charge required for the formation of a monolayer (in this case, q = 257 $\mu C/cm^2$ was considered). It was calculated an electrochemical active surface of 3.9 m^2/g, higher than ~1.2 m^2/g reported in literature for Ni catalyst [25-26]. In the urea solution there is a small oxidation potential at ~700mV and a maximum current densities of 12 mA/cm^2 corresponding to urea oxidation at Ni catalyst site (Fig. *2* (2)), values that are considerable higher than in the case of Pt/C catalyst (Figure 2(3) respective Figure 2(4). In addition a high double layer capacitance (Figure 2(4)) in urea solution will hinder the urea oxidation and in consequence a slow yield.

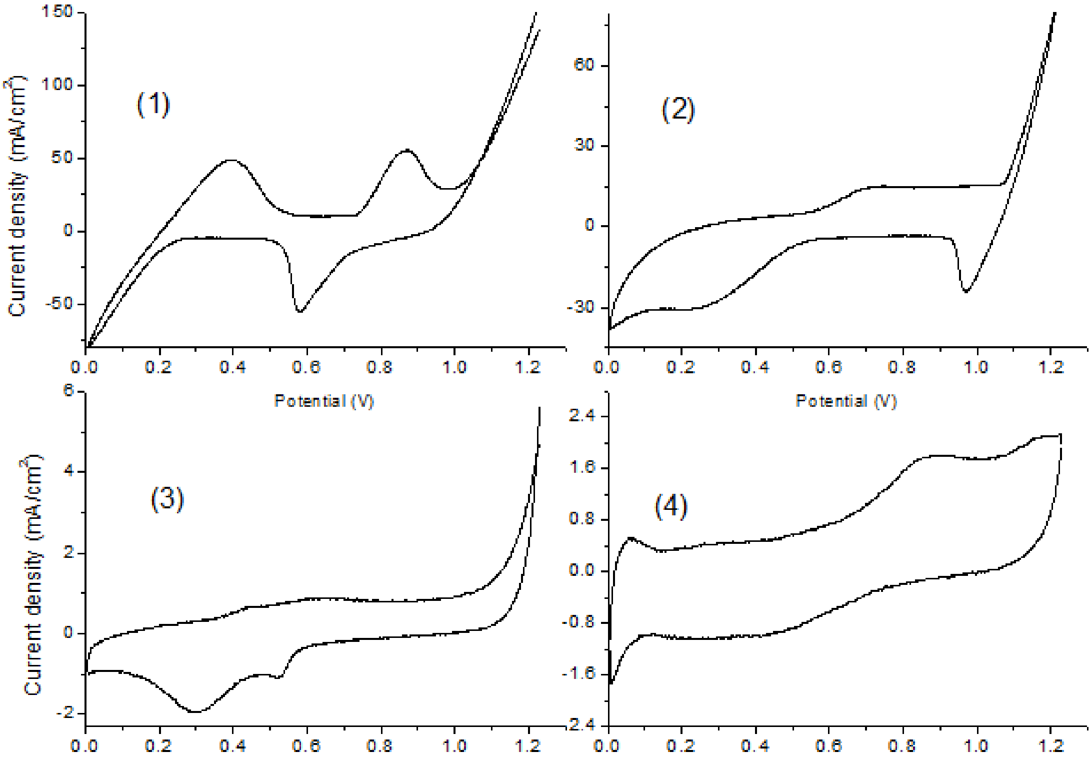

Fig. 2. Cyclic voltammetry performed at scan rate 100mV/s, reference electrode DHE. 1) Ni/MWCNTs in 5.5 M KOH solution 2) Ni/MWCNTs in 3.7 M KOH+0.33 M urea 3) Pt catalyst in 5.5 M KOH solution 4) Pt catalyst in 3.7 M KOH+0.33 M urea.

3.2 MEA Tests

The performance and power density curves for two different MEA configurations containing a proton exchange membrane and Pt/C or Ni/MWCNTs as anode catalysts, while Pt/C was used as cathode catalyst are shown in

Fig. *3* and, respectively in Fig 4.

Table 3. Urea- hydrogen peroxide FC performances.

.	Membrane	Anode		Cathode		UFC performances		
		Catalyst (mg/cm^2)	Fuel	Catalyst (mg/cm^2)	Oxidant	OCV (mV)	J $_{SC}$ (mA/ cm^2)	P$_{max}$ (μW/ cm^2)
1	Fumapem F1050	Pt/C (0.6)	1M urea +1.5M NaOH	Pt/C (0.6)	20% H_2O_2 +5% H_3PO_4	361	0.32	29
2	Fumapem F1050	Ni/ MWCNTs (10)	1M urea +1.5M NaOH	Pt/C (1)	20% H_2O_2 +5% H_3PO_4	262	0.80	56

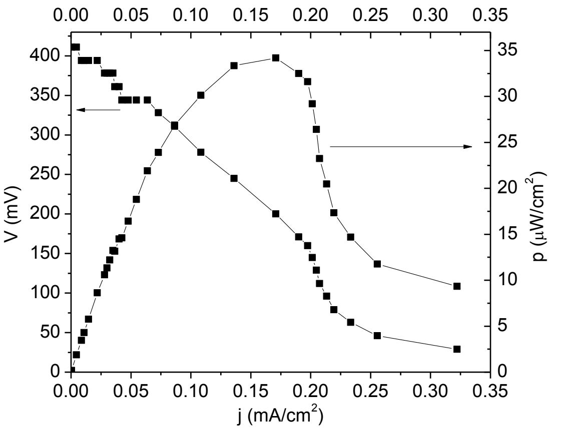

Fig. 3. Current density–voltage and current density–power density curve for MEA 1 (membrane: Fumapem F1050; anode catalyst: Pt/C 0.6 mg/cm^2; cathode catalyst: Pt/C 0.6 mg/cm^2)

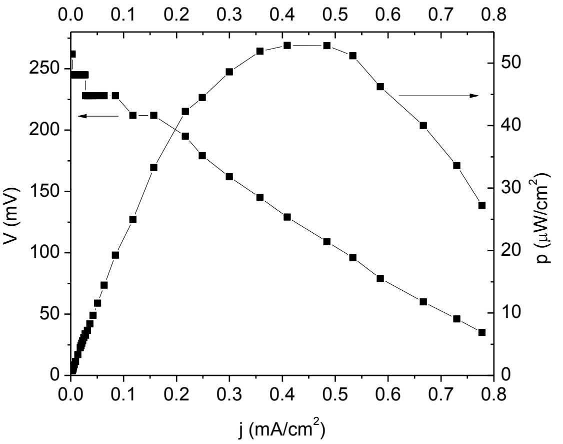

Fig 4. Current density–voltage and current density–power density curve for - MEA 2 (membrane: Fumapem F1050; anode catalyst: Ni/MWCNTs 10 mg/cm^2; cathode catalyst: Pt/C 1 mg/cm^2)

Polarization curves were studied for a couple fuel -oxidant: urea solution- hydrogen peroxide. The open circuit potential (OCV) of the fuel cell with Pt/C anode catalyst was 0.36 V, higher than 0.26 V observed on the fuel cell with Ni/MWCNTs anode catalyst. On the other hand, the Ni/MWCNTs cell achieved a peak power density of 56 μW/cm^2, which is much higher than 29 μW/cm^2 measured on the Pt/C cell, as summarized in

Table *3*. The performance of Ni/MWCNTs cell is improved by 52%. The higher performance is ascribed to the high Ni catalyst efficiency as shown in Fig. *2*, but also to the CO poisoning of Pt catalyst. The results in the present study demonstrate that the electrocatalyst type has significant influence on the cell performance.

3.3 Corrosion ware

Corrosion of fuel cell components and degradation of MEA occurs after performing fuel cell specific tests. Both the 20% hydrogen peroxide and 5% H_3PO_4 solution used as cathode oxidant and the 1 M urea and 1.5 M NaOH solution at the anode side are producing corrosion of metal fastenings and bolts. Resulting oxides and salts reach into the reactant solutions affecting the proper operation of the fuel cell. For this reason, the experimental fuel cell model used in laboratory tests must be redesigned with only non-metallic materials: Plexiglas, Teflon.

3.4 Gaseous by-products identification

During experiments, it was observed the formation of gaseous products, which were collected and analysed using a residual gas analyser. N_2 and CO_2 gaseous by-products are formed during urea-hydrogen peroxide fuel cell reactions. Residual gas analysis revealed N_2 and O_2 presence, while almost no CO_2 was found, as shown in Fig. 5. The unexpected O_2 presence is most likely due to the decomposition of hydrogen peroxide and diffusion through the separation membrane.

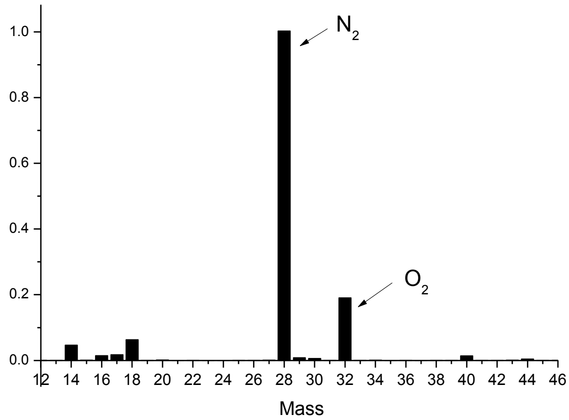

Fig. 5. Analysis of gaseous by-products resulted from urea-hydrogen peroxide fuel cell reactions.

On the other hand, CO_2 absence from the gaseous product spectrum is the result of NaOH reaction with CO_2, occurring at the anode side. Reaction products are Na_2CO_3 and/or $NaHCO_3$, according to the following reaction equations:

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$
$$Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$$

This hypothesis is supported by mass spectrometry analysis of the anode solution at the end of the experiments, which proves the presence of $NaHCO_3$. Mass spectrometry analyses using negative ionization of the anolyte solution used in UFC shows a distribution of specific ions present in sodium hydrogen carbonate solution. Mass spectrometry analyses on 0.1M $NaHCO_3$ solution revealed negative representative ions with: 141, 223, 305, 387 m/z.

4. Conclusions

The present study tested the hypothesis of generating electricity directly from urea when considering hydrogen peroxide as oxidant in a urea fuel cell. For this purpose, Pt/C or Ni/MWCNTs catalysts where tested for urea oxidation at anode site. Polarization curves obtained for urea solution- hydrogen peroxide as fuel -oxidant couple revealed a two times higher maximum power density for Ni/MWCNTs catalyst than for Pt/C catalyst. Urea electro oxidation resulting gases were identified as N_2 and CO_2. Gaseous by-products collected during experiments contained mostly nitrogen and oxygen in a 5: 1 ratio, while CO_2 formation was identified indirectly as sodium hydrogen carbonate in the anode solution as a result of its reaction with NaOH. Further studies are to be conducted in developing the appropriate catalyst couples for improving urea- hydrogen peroxide fuel cell performances.

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