Electronic Supplementary Information

for

Membraneless Hydrogen Peroxide Micro Semi-Fuel Cell for Portable Applications

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Electrochemical Characterization

Electrodes were connected to an electric load system (Solartron Analytical, Solartron Group Limited, UK), using alligator clips. The results were evaluated with the MultiStat electrochemistry software (Scribner Associates Inc., USA). A potential scanning rate of 20 mV/s with a potential step of 20 mV was set for I-V and CV experiments. The characterization was carried out at room temperature of 25°C.

Anode was made of Aluminium or Magnesium strip with dimensions of 5 mm×10 mm. While both sides of the anode were exposed to the solution, a total surface area of 1 cm^2 was obtained. Cathode surface area was 1 cm^2 with dimensions of 8 mm×12.5 mm.

Open-circuit potential

For all fabricated cells, the open-circuit potential (OCV) was monitored for 10 minutes before the I-V test.

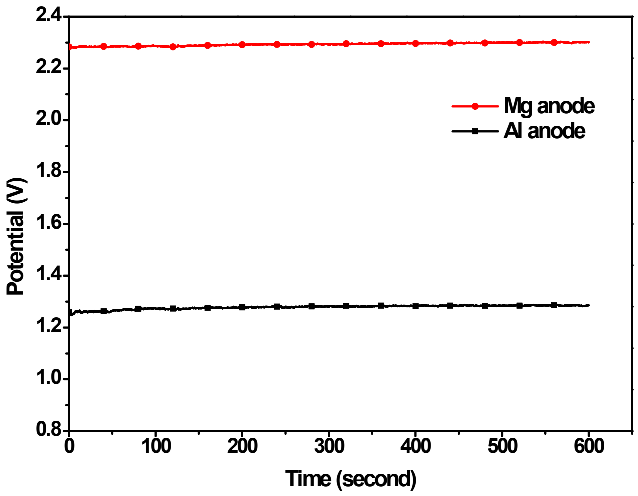


Fig S1 Open-circuit potential of a cell with Mg anode and Al anode. Cathode was PB-coated carbon paper. Solution in the reservoir ~~is~~ was 2mL 0.5 M H_2O_2 in 0.1 M HCl.

Linear sweep voltammetry experiment

In addition to characterizing the device using a 2-ml fuel reservoir, fuel cells with Mg and Al electrodes were characterized in a 100-ml beaker containing 0.1 M HCl with and without H_2O_2. For fuel cell with Mg anode, maximum power density of up to 7.5 mW cm^{-2} was achieved.

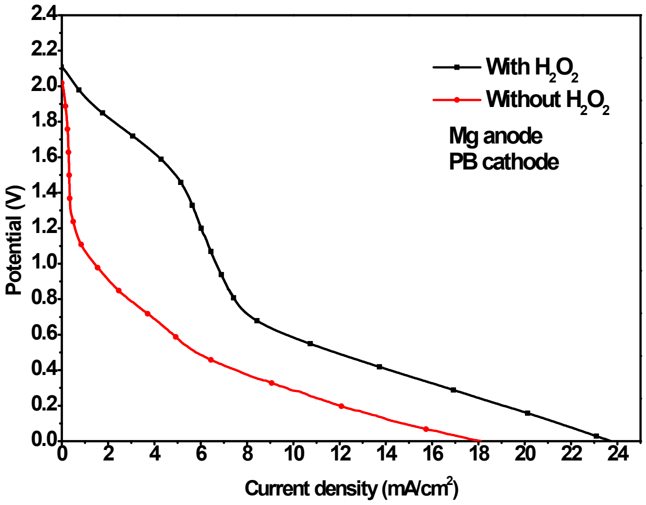


Fig S2 Linear sweep voltammetry of a cell with Mg anode. Cathode was a PB-coated carbon paper. Electrodes were immersed in a 100 ml beaker containing 50 mL of 0.1 M HCl with and without 0.5 M H_2O_2.

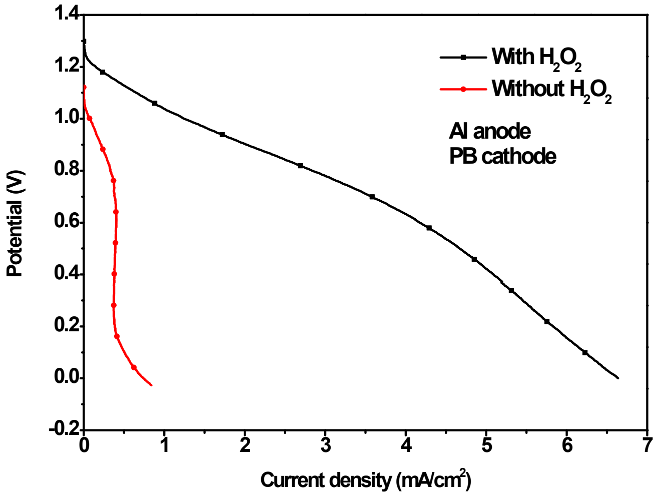


Fig S3 Linear sweep voltammetry of a cell with Al anode. Cathode was PB-coated carbon paper. Electrodes were immersed in a 100 ml beaker containing 50 mL of 0.1 M HCl with and without 0.5 M H_2O_2.

Chronoamperometry experiment

In order to evaluate the long term performance of the cell, solution containing H_2O_2 and the supporting electrolyte was changed for a few times and chronoamperometry experiments were repeated. It was observed that the results are quite repeatable with the same trend.

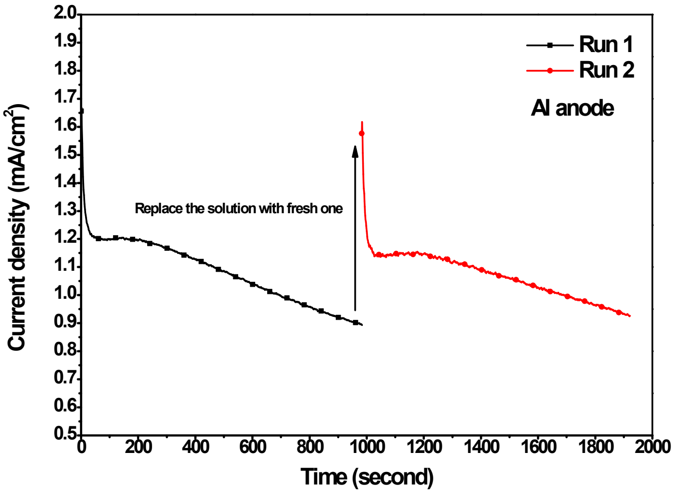


Figure S4 Chronoamperometry test for fuel cell with Al anode and PB cathode. Solution in the reservoir, 2ml of 0.5 M H_2O_2 with 0.1 M HCl.

Cell reactions

The electrochemical reaction taking place at the cathode side of the Al and Mg semi-fuel cells is the electro-reduction of hydrogen peroxide at the Prussian blue electrode.

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O; \quad E^0 = 1.77\text{ V} \qquad \text{(S1)}$$

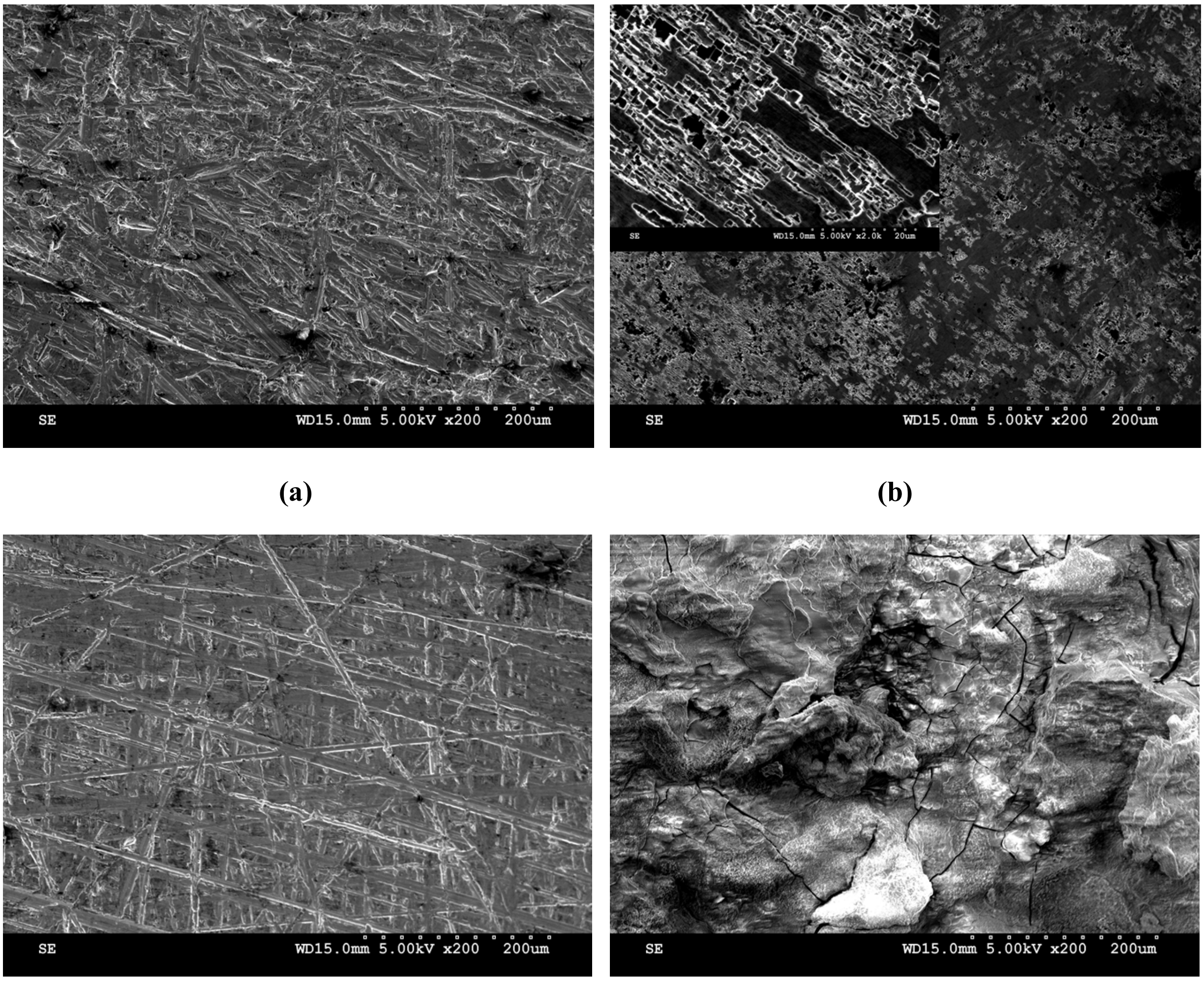
The anode reactions for the Mg and Al semi-fuel cells are presented in Table S1. The electrochemical reactions include the electro-oxidation reaction of hydrogen peroxide and the electro-oxidation of the metal (Mg and Al) electrode. In addition, hydrogen evolution takes place at the metallic electrodes imposing a potential loss due to mass transport. As mentioned, there are some side reactions taking place in the cell which cause a significant drop in the cell potential. In the case of aluminium, these reactions include the corrosion of aluminium, secondary chemical reactions happening in the acidic environment, direct reaction of aluminium with hydrogen peroxide and the decomposition of hydrogen peroxide as presented in Table S1.[1, 2]

Table S1 The anode reactions for the Mg and Al semi-fuel cells

Semi-fuel cells			
Mg		**Al**	
Description	**Reaction**	**Description**	**Reaction**
Electrochemical reactions	$H_2O_2{}_{(aq)} \rightarrow O_2{}_{(g)} + 2H^+{}_{(aq)} + 2e^-$ $Mg_{(s)} \rightarrow Mg^{2+}{}_{(aq)} + 2e^-$; $E^0=2.37$ V $2H^+{}_{(aq)} + 2e^- \rightarrow H_2{}_{(g)}$	Electrochemical reactions	$H_2O_2{}_{(aq)} \rightarrow O_2{}_{(g)} + 2H^+{}_{(aq)} + 2e^-$ $Al_{(s)} \rightarrow Al^{3+}{}_{(aq)} + 3e^-$; $E^0=1.66$ V $2H^+{}_{(aq)} + 2e^- \rightarrow H_2{}_{(g)}$
Corrosion	$Mg_{(s)} + 2H_2O_{(l)} \rightarrow Mg(OH)_{2(s)} + H_{2(g)}$	Corrosion	$2Al_{(s)} + 6H_2O_{(l)} \rightarrow 2Al(OH)_{3(s)} + 3H_{2(g)}$
	$Mg_{(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2(s)} + H_2{}_{(g)}$		$2Al_{(s)} + 6HCl_{(aq)} \rightarrow 2AlCl_{3(s)} + 3H_{2(g)}$
Direct reaction	$Mg_{(s)} + H_2O_{2(aq)} \rightarrow Mg(OH)_{2(s)}$	Secondary chemical reactions	$Al^{3+}{}_{(aq)} + 3Cl^-{}_{(aq)} \rightarrow AlCl_3{}_{(s)}$ $AlCl_{3(s)} + 3H_2O_{(l)} \rightarrow Al(OH)_{3(s)} + 3HCl_{(aq)}$
Decomposition	$2H_2O_2{}_{(aq)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$	Direct reaction	$2Al_{(s)} + 3H_2O_{2(aq)} \rightarrow 2Al(OH)_{3(s)}$
		Decomposition	$2H_2O_2{}_{(aq)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$

The corrosion reaction consumes the anode material and formation of hydrogen gas reduces the availability of active sites for the electrode. In the case of aluminium, the corrosion and direct reaction produce a thin layer of $Al(OH)_3$ on the electrode which hinders further corrosion.[2] The decomposition of hydrogen peroxide takes place at the electrodes and produces water and oxygen. The produced oxygen bubbles contribute to further losses. Figure S5 show SEM images of Al and Mg electrodes before and after running the fuel cell.

It is worth mentioning that the amount of Mg and Al ions present in the solution was measured using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) instrument, after chronoamperometry test. The average quantity for Al and Mg were 4.54 mg/l and 49.6 mg/l.



(a) **(b)**

(c) **(d)**

Figure S5 SEM images of anode: (a) Al electrode (plain) before immersion in the solution, (b) Al electrode after immersion in the solusion and running the fuel cell; (c) Mg electrode (plain) before immersion in the solution; (d) Mg electrode after immersion in the solusion and running the fuel cell. Scratches seen on electrodes at (a) and (c) are because of polished surface by sand paper, grade 1000.

In order to investigate the electrochemical oxidation of hydrogen peroxide on the electrode surface, cyclic voltammetric tests are carried out. The obtained voltammograms are presented in Figure S6. It can be seen that the current peak happens in the reverse scan. While, the current produced in the forward scan is too low. The peak current in the reverse scan is proposed to be due to the re-oxidation of the electrode after the oxide film formed in the forward scan has been electro-reduced by hydrogen peroxide [3, 4]. The low current in the forward scan is explainable by the fact that both the potential and current are highly dependent on the pH of the solution as protons are engaged in the oxidation process. Lower pH values correspond to higher proton concentrations hindering the oxidation of hydrogen peroxide. Furthermore, the presence of chloride ions and probably Nafion in the solution inhibits the oxidation of hydrogen peroxide [5].

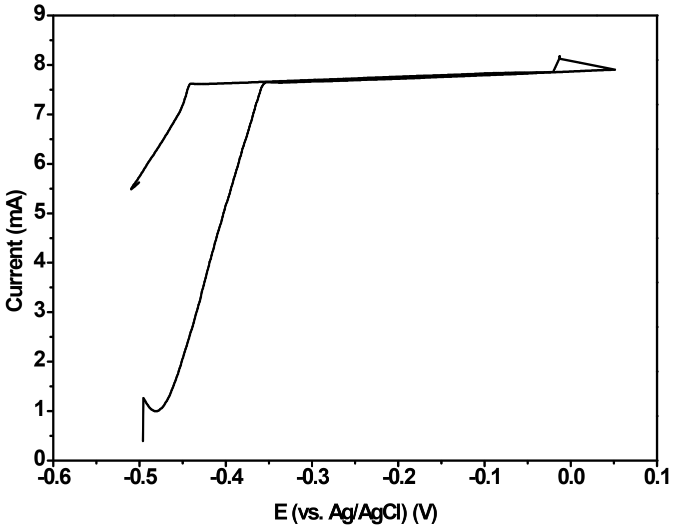


Figure S6. CV graph for Aluminium in 0.1 M HCl with 0.5 M H_2O_2.

References:

1. E. Ghali, *Corrosion Resistance of Aluminum and Magnesium Alloys: Understanding, Performance, and Testing*, 2010.
2. C. Vargel, M. Jacques and M. Schmidt, *Corrosion of Aluminium*, Elsevier 2004.
3. Roberts, J.G., K.L. Hamilton, and L.A. Sombers, *Comparison of electrode materials for the detection of rapid hydrogen peroxide fluctuations using background-subtracted fast scan cyclic voltammetry.* Analyst, 2011. **136**(17): p. 3550-3556.
4. Hall, S.B., E.A. Khudaish, and A.L. Hart, *Electrochemical oxidation of hydrogen peroxide at platinum electrodes. Part IV: Phosphate buffer dependence.* Electrochimica Acta, 1999. **44**(25): p. 4573-4582.
5. Hall, S.B., E.A. Khudaish, and A.L. Hart, *Electrochemical oxidation of hydrogen peroxide at platinum electrodes. Part V: Inhibition by chloride.* Electrochimica Acta, 2000. **45**(21): p. 3573-3579.