The Electrochemical Generation of Ozone using an Autonomous Photovoltaic System

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An autonomous photovoltaic system was used as the power supply for a proton-exchange membrane (PEM) electrochemical cell for electrochemically generated ozone supplying the necessary current at a voltage high enough to allow the ozone generation besides the normal water electrolysis process. This system may be used as a portable device for water disinfection (limited amounts) in regions where the electricity is not easily available and the quality of drinking water needs improvement providing the required ozone concentration for pathogen inactivation.

Keywords: ozone autonomous photovoltaic system, PEM, electrochemical cell

A World Health Organisation and UNICEF report estimates that over 2.6 billion people in the world do not have access to sanitation facilities and 884 million people lack access to clean drinking water [1]. In the recent years, tertiary treatment has gained attention as a result of population growth and increase of water request.

Tertiary water treatment requires the use of disinfecting agents (usually chlorine compounds) [2] in order to inactivate pathogens and it is usually accomplished after a proper secondary wastewater treatment [3]. Although chemical disinfection is efficient and prevents water recontamination, the side reactions that occur in aqueous media can lead to the formation of some unwanted compounds, the so-called disinfection by-products [2, 4-10]. Studies now focus on alternative disinfection methods [11], less expensive. Among these, the use of ozone is by far the most suitable method for tertiary water treatment. During ozonation, no harmful by-products are produced [3, 12] and the dissolved oxygen concentration increases, so the aeration is no longer required [3]. Moreover, ozone is a strong oxidizing agent (it has an oxidation potential of 2.07V) [12-16] and it is effective in the removal of trace levels of pharmaceuticals, fragrances and estrogens [17], degradation of atrazine [18] and some endocrine disruptors [19] and in the discoloration of dye Reactive Orange 122 [20], Orange-13 and Blue-19 [21]. As drawbacks of ozonation, one mentions the ozone short half-life [13, 15] and higher capital costs [3] compared to alternatives.

Usually, ozone is generated by Corona discharge or through electrolysis [2, 14]. Of the advantages of electrochemical production, one notices higher ozone concentration compared to corona discharge [14] and the direct generation of ozone in the aqueous media [22]. The main drawbacks of electrolytic process are the elevated energy consumption [14], the use of unstable electrode materials [2, 22] and the complexity of production systems [22].

Factors affecting the performance of the electrolytic process are electrode material [11, 12], nature and composition of the electrolyte [11, 12, 23] and operating parameters (such as *p*H value, temperature, applied voltage) [11].

From the electrochemical point of view, the ozone is generated besides oxygen at the anode of the electrolytic cell and hydrogen is produced at the cathode. The equations describing the above said electrolytic process are [2, 12, 13, 24-26]:

$$3H_2O \rightarrow O_3 + 6H^+ + 6e^-,\ E^0 = 1.52V \qquad (1)$$

$$2H^+ + 2e^- \rightarrow H_2, E^0 = 0V \qquad (2)$$

The ozone generation reaction is a side reaction and competes with oxygen evolution reaction, the later being thermodynamically favoured [2, 12-14, 24-26]:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-,\ E^0 = 1.23V \qquad (3)$$

Usually, the electrodes used in the electrolytic process have a high oxygen overpotential [12, 22]. Among these electrodes, one mentions the ones made of platinum [12], boron-doped diamond [26], PbO_2-loaded Pt screens [27], Ti/β-PbO_2 [18, 28], silicon / titanium oxide / platinum / titanium dioxide (Si/TiO_x/Pt/TiO_2) [12, 13], Pt–TaO_x/Ti [24], Ni–Sb–SnO_2/Ti [25] and tantalum oxide [29].

The purpose of this paper was to produce a portable autonomous photovoltaically driven system used in conjunction with a modified PEM electrochemical cell for electrochemically generated ozone that can be used for drinking water disinfection.

Experimental part

In our particular case, the ozone generation was performed in a modified PEM electrolyser used in conjunction with a duplex solar charger fitted with a Li-Ion rechargeable battery as back-up, type SE 1500 model 1 GW-457832 (China). Moreover, one has tested two other chargers, namely MIPOW Powertube 2200 and Mobile Power Bank 3600, China.

The electrolyser was manufactured starting from a Thames and Kosmos X7-628777 PEM fuel cell (Germany), replacing the original platinum - Nafion - platinum membrane electrode assembly (MEA) prone to electrode fouling/poisoning with one consisting of two identical 37mm x 37mm x 1mm perforated (100 holes x 2 mm inner diameter) Ti electrodes plates (William Gregor Ltd., UK) and a proton exchange membrane (PEM), namely Nafion® 117 (DuPont, USA). The membrane was activated

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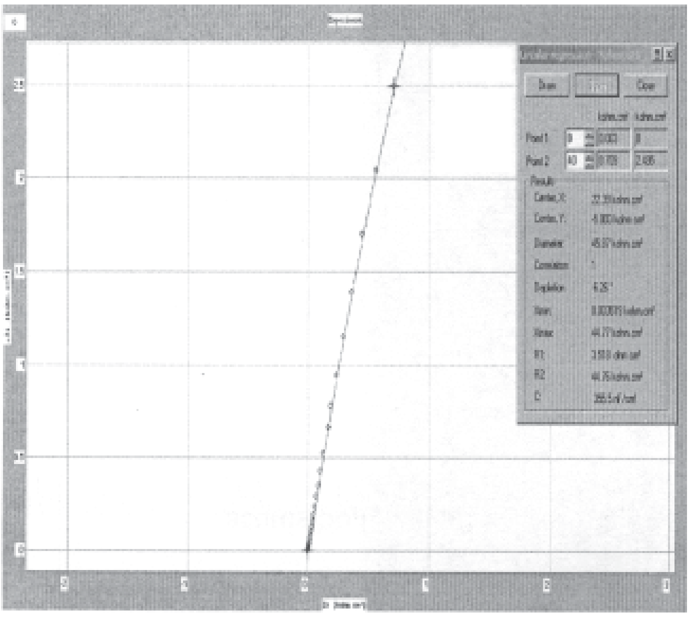

Fig. 1. A captured screen of the Nyquist diagram for Nafion® 117

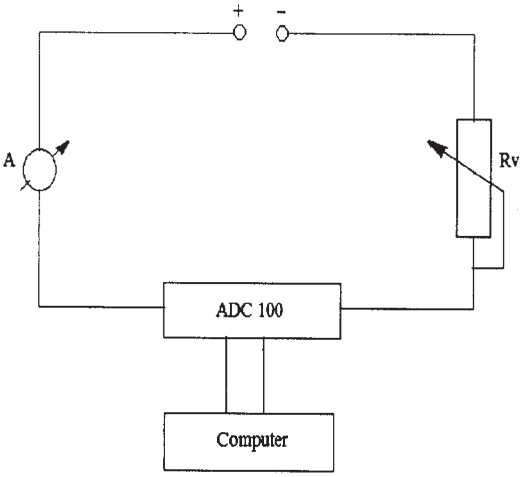

Fig. 2. The scheme used for the solar charger testing: A- ammeter, R_V- variable resistance, ADC 100 – analogue digital converter and digital acquisition system

and hydrated according to the following procedure: pretreatment at 80°C in 3%wt H_2O_2 for 2h, followed by cooling and washing with bidistilled water. The membrane was kept in 0.5 M H_2SO_4 for 48h. After 48h, the membrane is washed with bidistilled water and boiled in 0.02M H_2SO_4 for 1h. Finally, the membrane is washed with bidistilled water. Following the activation, the membrane was stored in bidistilled water, at room temperature.

Once activated and hydrated, the membrane was tested for the determination of the ionic conductivity using the electrochemical impedance spectroscopy (VoltaLab 40/ PGZ 301 Dynamic Electrochemical System, Radiometer, France) used in conjunction with a platinum based parallel opposed dual electrode cell (0.95cm^2 active common surface) fitted between the vise of a Mitutoyo (Japan) digital micrometer, the membrane playing the role of a solid electrolyte for this cell. In this way, one is now able to determine precisely the membrane thickness (of a paramount importance) during the electrochemical impedance measurements. This technique, particularly applicable for PEM is described in details elsewhere [30-32].

The associated electrochemical impedance spectroscopy frequency was between 100 kHz and 1 Hz using a potential amplitude perturbation of 10 mV. The integrated data processing software allows for a circular regression procedure and hence the value of the ionic conductivity is now determined from the Nyquist normalised real impedance value, R1, (ohm·cm^2), resulting from intersection of the real impedance axis in the high frequency area of EIS plot and the actual value of the membrane thickness displayed on the digital micrometer during the electrochemical impedance measurements:

$$\mu = \frac{h}{R1} \tag{4}$$

where:μ is the ionic conductivity, ohm^{-1}·cm^{-1}, h is the measured membrane thickness, cm and R1-the intersection of experimental curve with the real impedance axis, ohm·cm^2, (fig. 1).

By processing the data one has obtained for a Nafion® 117 membrane thickness of 189μm (manufacturer data suggest 183μm) and taking into account the value of R1 = 3.518 ohm·cm^2 calculated following the regression procedure supplyed by the Voltalab 40 associated software, the calculated ionic conductivity value for the PEM was 0.00537 ohm^{-1}·cm^{-1} (the value of the regression correlation coefficient was 0.9999 out of 40 points). This value, somehow lower than the normal ionic conductivity range for Nafion® 117 (0.01 – 0.1 ohm^{-1}·cm^{-1}) may be explained by the fact that the membrane is partially loosing water when squeezed between the vise of the micrometer.

The membrane was inserted into the PEM cell, and the cell was assembled using the Ti electrodes.

In order to determine the minimum necessary electrolysis voltage for the ozone generation, the electrolyser was initially tested using a laboratory power supply (Labornetzgeraet LN-103pro, MCI Power, Germany) that allows the electrical power to be delivered at a constant voltage regardless of the variation of the ohmic drop, starting from 1.3 V increasing in 0.1 V steps, the voltage being measured with a digital voltmeter (KT115, Kewtech Corporation, Japan). The anode gas tube inserted into a gas collector filled with a 150 mL distilled water, allowing the anode reaction products to be sparged in water as only the dissolved ozone is of interest (the cathode/hydrogen tube was left in air). It was found that the minimum necessary voltage for the ozone generation so that it can be sensed using Sensafe (USA) disposable test strips for the dissolved ozone was 2.2 V and this was considered a threshold for ozone generation for this particular system.

The solar charger was tested using a standardised charging/discharging procedure, the charging taking place at a constant current (0.5 A). An initial discharging process took place at a current value of 0.33 A. In this particular case, the discharging took place at a value slightly lower than that used during the electrochemical generation of ozone, namely 0.5A.

The experimental layout is depicted in figure 2.

The system uses a computer controlled digital acquisition system (Picolog ADC 100, PicoTechnology, UK), a variable discharge resistor, to allow the current to be kept constant while the voltage decreases, and a digital ammeter (LCR-Multimeter 4095, Voltcraft, Germany).

During the discharge, the solar panel was completely blocked/covered to prevent the charging of the back-up battery.

Results and discussions

The results obtained during the discharge procedure for the rechargeable battery/solar charger are shown in figures 3 and 4 in the form of a polarization curve versus time.

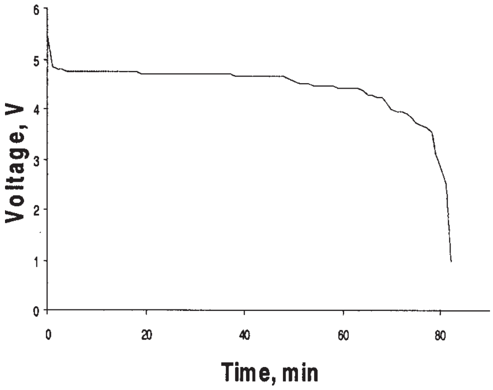

Fig. 3. The discharge diagram for the solar charger (for a discharge current of 0.33 A)

Table 1
EXPERIMENTAL VALUES OF EACH CHARGER CAPACITY

Charger type	Discharge time, h	Capacity, mAh
SE 1500 model 1 GW-457832	0.5	250
MIPOW Powertube 2200	1.68	840
Mobile Power Bank 3600	4.83	2415

Once each charger was evaluated, the laboratory power supply previously used for the determination of the minimum electrolysis voltage was replaced with each of these chargers, fully charged, and the electrolyser was connected to each of them, the circuit also containing a digital ammeter (LCR-Multimeter 4095, Voltcraft, Germany) connected in series with the cell, allowing the current monitoring and a digital voltmeter (KT115, Kewtech Corporation, Japan), connected so that the voltage can also be recorded.

The experimental values of each charger capacity for the above said current value are presented in table 1.

Once the solar charger was evaluated, the laboratory power supply used previously for the determination of the minimum electrolysis voltage was replaced with the solar charger, fully charged, and the electrolyser was connected to it, the circuit also containing a digital ammeter (LCR-Multimeter 4095, Voltcraft, Germany) connected in series with the cell, allowing the current monitoring and a digital voltmeter (KT115, Kewtech Corporation, Japan), connected in parallel so that the voltage can also be recorded.

The experimental values of each charger capacity for the above said current value are presented in table 1.

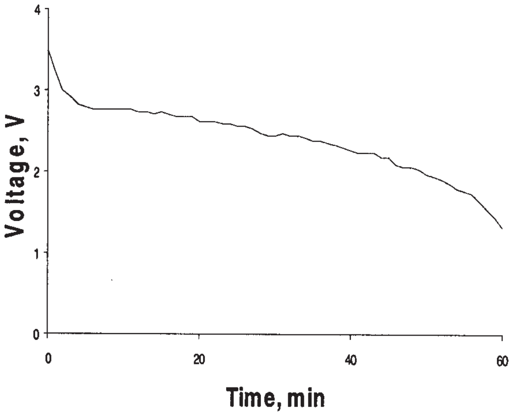

Fig. 4. The discharge diagram for the solar charger (for a discharge current of 0.5 A)

Table 2
CONCENTRATION OF GENERATED OZONE AND THE VALUES OF THE OPERATING PARAMETERS

Time, Min	Voltage, V	Current intensity, A	Dissolved ozone concentration, C_{O_3}, mg·L^{-1}
3	2.74	0.48	0.05
6	2.72	0.47	0.1
9	2.70	0.47	0.1
12	2.68	0.47	0.1
15	2.67	0.46	0.1
18	2.67	0.46	0.1
21	2.66	0.45	0.2
24	2.65	0.45	0.2
27	2.64	0.45	0.2
30	2.62	0.44	0.2

The anode gas tube inserted into gas collector filled with 150 mL water (the cathode/hydrogen tube was left in air) and the electrical circuit switched on. The system starts generating a mixture of oxygen and ozone at anode and hydrogen at cathode. Although the system generates more ozone than the amount quantified as dissolved ozone, only the dissolved ozone concentration was measured using Sensafe (USA) disposable ozone test strips, part of the ozone being released into atmosphere alongside with the remaining undissolved oxygen.

The attempt to collect the ozone in a pressurised container, although works in the case of the laboratory power supply, does not work well with the solar charger, where increased power is necessary to compensate the backpressure responsible for shifting the equilibrium in favour of water formation rather than ozone/oxygen and hydrogen formation.

The recorded values of current and voltage during the operation of the cell connected to the solar charger indicate a maximum current intensity of 0.48 A and an output voltage of 2.74 V (table 2). Under these conditions, the maximum dissolved ozone concentration is 0.2 mg·L^{-1} after 30 min electrolysis time. This value is much higher than the one necessary for pathogen inactivation (0.008 mg·L^{-1}) [33].

The results showed that the solar charger can run for 30 min before reaching the switched off discharged state and it provides the voltage and current necessary for the electrogeneration of a quantity of ozone able to sterilise 0.150 x 0.2/0.008 = 3.75 L water/30 min.

One should mention that the evaluation was carried out using only the back-up battery the solar panel being completely blocked to prevent the charging of the back-up battery during the experiments, the worst possible scenario (night time operation). If the solar panel is exposed to daylight, then the total operation time is extended, the current load being now partially supplied by the photovoltaic cells, extending the discharge time for the rechargeable battery.

Should anyone require an extended period of operation, then it is advisable to use Mobile Power Bank as it offers about 5h of operation, so that one has now an increased authonomy, about ten times more than with the initial power supply before its complete discharging. Thus, the total quantity of ozone generated after 4.5h is able to sterilise 33.75 L water.

Moreover, this particular charger can be interconnected with the solar power charger in order to top up with some extra electrical energy and/or recharge it during the daytime.

Conclusions

An autonomous power system based on a solar charger and a Li-Ion rechargeable battery was used as the main power supply for the electrogeneration of ozone in a modified PEM cell.

The solar charger provides the necessary autonomy for the electrochemical process to take place for at least 30 minutes for normal operation. The results proved that the system may be able to sterilise up to 3.75 L/30 min before being recharged, the dissolved ozone concentrations being high enough to inhibit and prevent microbial growth.

Moreover, the autonomy may be improved by using two other chargers, namely MIPOW Powertube 2200 and/or Mobile Power bank 3600, which provide an operating time of 100 min and 290 min, respectively, the total quantity of ozone generated after 1.5h and respectively 4.5h being able to sterilise 11.25, respectively 33.75 L of drinking water.

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References

1. WORLD HEALTH ORGANISATION and UNICEF, Progress on sanitation and drinking water, WHO/UNICEF Joint Monitoring Programme for Water Supply and Sanitation, WHO Press, Geneva, 2010;
2. KRAFT, A., Platinum Met Rev, **52**, 2008, p. 177;
3. UNITED STATES ENVIRONMENTAL PROTECTION AGENCY, Wastewater technology fact sheet: ozone disinfection, 1999, available online at: http://water.epa.gov/scitech/wastetech/upload/2002_06_28_mtb_ozon.pdf;
4. SADIQ, R., RODRIGUEZ, M.J., Sci Total Environ, **321**, 2004, p. 21;
5. GOPAL, K., TRIPATHY, S.S., BERSILLON, J.L., DUBEY, S.P., J Hazard Mater, **140**, 2007, p. 1;
6. HRUDEY, S.E., Water Res, **43**, 2009, p. 2057;
7. HUA, G., RECKHOW, D.A., Water Res, **41**, 2007, p. 1667;
8. AGUS, E., VOUTCHKOV, N., SEDLAK, D.L., Desalination, **237**, 2009, p. 214;
9. MOSTEO, R., MIGUEL, N., MARTIN-MUNIESA, S., ORMAD, M.P., OVELLEIRO, J.L., J Hazard Mater, **172**, 2009, p. 661;
10.CHANG, E.E., CHIANG, P.C., CHAO, S.H., LIN, Y.L., Chemosphere, **64**, 2006, p. 1196;
11. JEONG, J., KIM, C., YOON, J., Water Res, **43**, 2009, p. 895;
12. KITSUKA, K., KANEDA, K., IKEMATSU, M., ISEKI, M., MUSHIAKE, K., OHSAKA, T., Electrochimica Acta, **55**, 2009, p. 31;
13. MOHAMMAD, A.M., KITSUKA, K., ABDULLAH, A.M., AWAD, M.I., OKAJIMA, T., KANEDA, K., IKEMATSU, M., OHSAKA, T., Appl Surf Sci, **255**, 2009, p. 8458;
14. SANTANA, M.H.P., DE FARIA, L.A., BOODTS, J.F.C., Electrochimica Acta, **49**, 2004, p. 1925;
15. SHAMMAS, N.K., WANG, L.K., Handbook of Environmental Engineering,
Volume 3: Physicochemical Treatment Processes, **vol. 3**, The Humana Press Inc., WANG, L.K., HUNG, Y.T., SHAMMAS, N.K. (Editors), Totowa, NJ, 2004, p. 316
16. HEIM, C., GLAS, K., Brewing Science, **64**, 2011, p. 8
17. TERNES, T.A., STÜBER, J., HERRMANN, N., MCDOWELL, D., RIED, A., KAMPMANN, M., TEISER, B., Water Res, **37**, 2003, p. 1976
18. VERA, Y.M., DE CARVALHO, R.J., TOREM, M.L., CALFA, B.A., Chem Eng J, **155**, 2009, p. 691;
19. NING, B., GRAHAM, N.J.D., ZHANG, Y., Chemosphere, **68**, 2007, p. 1163
20. SANTANA, M.H.P., DA SILVA, L.M., FREITAS, A.C., BOODTS, J.F.C., FERNANDES, K.C., DE FARIA, L.A., J Hazard Mater, **164**, 2009, p. 10;
21. CHEN, T.Y., KAO, C.M., HONG, A., LIN, C.E., LIANG, S.H., Desalination, **249**, 2009, p. 1238
22. KRAFT, A., STADELMANN, M., WÜNSCHE, M., BLASCHKE, M., Electrochem Comm, **8**, 2006, p. 883
23. FRANCO, D.V., DA SILVA, L.M., JARDIM, W.F., BOODTS, J. F. C., J Braz Chem Soc, **17**, 2006, p. 746
24. AWAD, M.I., SATA, S., KANEDA, K., IKEMATSU, M., OKAJIMA, T., OHSAKA, T., Electrochem Comm, **8**, 2006, p. 1263;
25. BASIRIPARSA, J., ABBASI, M., J Solid State Electrochem, **16**, 2012, p. 1011
26. ARIHARA, K., TERASHIMA, C., FUJISHIMA, A., Electrochemical Solid-State Lett, **9**, 2006, p. D17
27. AWAD, M.I., SALEH, M.M., J Solid State Electrochem, **14**, 2010, p. 1877
28. DA SILVA, L.M., FRANCO, D.V., FORTI, J.C., JARDIM, W.F., BOODTS, J.F.C., J App Electrochem, **36**, 2006, p. 523
29. KANEDA, K., KITSUKA, K., NOWATAR, Y., IKEMATSU, M., ISEKI, M., HIGUCHI, T., HATTORI, T., TSUKAMOTO, T., ECS Transactions, **6**, 2008, p. 33
30. VAIREANU, D.I., MAIOR, I., GRIGORE, A., SAVOIU, D., Rev Chim. (Bucharest), **59**, no.10, 2008, p. 1140;
31. VAIREANU, D.I., COJOCARU, A., MAIOR, I., CAPRARESCU, S., Chem Bull "POLITEHNICA" Univ of Timisoara, Series Chemistry and Environmental Engineering, **53**, 2008, p. 258
32. VAIREANU, D.I., COJOCARU, A., MAIOR, I., CAPRARESCU, S., IONESCU, A., RADU, V., Key Eng Mater, **415**, 2009, p. 61
33. STANLEY, B.T., Electrolytic ozone generation and its application, available online at: http://www.degremont-technologies.com/IMG/pdf/tech_ozonia_pure_water.pdf.

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