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Long-term study of a new bioelectrochemical technology – The BioGenerator

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ABSTRACT

The BioGenerator is a unique microbial fuel cell for the conversion of hydrogen to electricity. It can be used in the hydrogen-based energy storage as a re-electrification device. This paper shows the results of the long-term stability testing of the BioGenerator. Using a bench scale bioreactor and electrochemical cell, it has been shown that the BioGenerator can achieve at least 3.8 years of continuous electricity generation without significant deterioration either in the biological or in the electrochemical components. The only part which was replaced twice a year was the anode in the electrochemical cell. The results of this work are a significant step towards the commercialization of the BioGenerator, especially in the energy storage sector.

Introduction

Hydrogen and energy storage

The conversion of hydrogen to electricity (cH2e) is a very important process which can have various applications [1]. There are different ways of converting hydrogen to electricity, however, at present only several of them are considered to be viable: burning hydrogen in combustion turbines; burning hydrogen in an internal combustion engine; combining hydrogen and oxygen electrochemically in fuel cells [2]. Unfortunately, in addition to their advantages, each of these three technologies has its own shortcomings. Firstly, due to very different physicochemical and thermodynamic properties of hydrogen in comparison with natural gas, there are significant difficulties in the design of such turbines [3]. Besides, their maximum efficiencies are expected to be within the range of 30% (for single cycle turbines) and 50% (for combined cycle turbines) determined based on the higher heating value (HHV) of hydrogen. Secondly, while there are existing internal combustion engines working with hydrogen as a fuel [4], their HHV efficiency is quite low – approximately 20–25%. Thirdly, despite the fact that the first hydrogen fuel cell (FC) automobile has recently been commercialized in Japan, hydrogen fuel cells for stationary large-scale applications have still been in the research and development phase [5], and their electrical efficiencies are expected to be up to 40% (HHV). Unfortunately, there is no profitable fuel cell company in the world yet [6]. Therefore, the main hurdles

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preventing the wide-spread use of cH2e converters include their technological development challenges and the relatively low efficiencies.

One of the most important applications of cH2e technologies is in the energy storage domain. It is well-understood that the transition from fossil-fuel to renewable primary energy sources is one of the paramount goals in the modern society mainly due to both environmental concerns, and logistical and geopolitical issues. Regrettably, the intermittency and unpredictability of the most common renewable energy sources, the wind and solar, drastically limit their ability for a direct integration into the existing electrical infrastructure [7]. The problems associated with renewable power variability can be solved by two main ways: a) - using back-up spinning reserves (mostly fossil-fuel-based); and b) - by using carbon-neutral energy storage technologies. It has been shown that the use of fossil-fuel-based spinning reserves results in significant greenhouse gas emissions [8], which completely obliterates the main advantage of the renewable power generation. Therefore, the development of carbon-neutral energy storage technologies is of tremendous importance for the successful development of renewable energy based economy. One of the most promising energy storage media is considered to be hydrogen [9,10]. The hydrogen-based energy storage contains three main components:

1. Generation of hydrogen by splitting water using the excessive electrical energy to be stored [11];
2. Storage of the produced hydrogen [12];
3. Conversion of the stored hydrogen back to electricity using a cH2e technology [10].

While the first two steps (water electrolysis and hydrogen storage) are relatively well-developed, the re-electrification (cH2e) is not quite yet, as discussed above.

The main objective of this work is to study the long-term stability of a unique bioelectrochemical convertor of hydrogen to electricity. It was named BioGenerator and is described below.

BioGenerator

As aforementioned, one of the most promising technologies for the cH2e is the fuel cell. As in other electrochemical electricity generation/storage devices (i.e. batteries), the fuel cells consist of two separated in space electrochemical half-reactions: one of them liberates electrons, for instance:

$$H_2 \rightarrow 2H^+ + 2e^- \quad (1)$$

and the other one consumes electrons:

$$½O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad (2)$$

When the electrodes of the above two reactions are connected by an electrical conductor, electrons start flowing from the point of production (reaction 1) to the point of consumption (reaction 2), thus generating electrical current. The above two reactions represent the electrochemistry in the most common acidic hydrogen/oxygen fuel cell such as the proton exchange membrane fuel cell. Due to the inherently sluggish kinetics of the considered reactions, both of them require electrocatalysts (usually platinum or platinum-based) to speed up the redox processes at the electrodes. Pt catalyst is especially important for the oxygen reduction (ORR) represented by Eq. (2) because it is slower than the hydrogen oxidation reaction (Eq. (1) by approximately 4 orders of magnitude [13]. However, the slowness of the reaction (2), even using a Pt electrocatalyst, is the main cause of the serious problems in PEM fuel cells, which include the high cost due to the large amounts of Pt; the relatively low stability due to the poisoning of Pt by impurities present in the atmospheric oxygen; as well as the low electrical efficiency due to the high cathodic overpotential.

Therefore, the performance of the H_2/O_2 fuel cells can be greatly improved if one can find a way to increase the rate of ORR without using precious-metal-based electrocatalysts [14].

It is a very well known fact that the oxygen-respiring living organisms (mammals and some microorganisms) assimilate oxygen according to the following biochemical reaction:

$$½O_2 + 2H^+ + 2e^- = H_2O \quad (3)$$

It is interesting to note that the overall respiration reaction (3) is very similar to the cathodic fuel cell reaction (2). However, there is one very distinct and important difference – the rate of the biological respiration (3) is by at least three orders of magnitude faster that the rate of the cathodic oxygen reduction reaction (2), even on Pt electrocatalyst, due to the extremely efficient biocatalysis in living organisms.

Therefore, since the low rate of the electrochemical ORR (Eq. (2)) is the main bottleneck in PEM fuel cells, and since the biological respiration reaction (3) occurs much faster in living organisms, the main idea behind the BioGenerator is to use the respiration of living organisms (microorganisms) in the cathodic oxygen reduction process.

In the BioGenerator [15], the iron-oxidizing microorganisms *Acidithiobacillus ferrooxidans* or *Leptospirillum ferriphilum* use the energy of oxygen reduction (respiration) to oxidize ferric to ferrous ions. The latter are then pumped into the cathodic compartment of an electrochemical cell where they serve as oxidant:

$$Fe^{3+} + e^- = Fe^{2+} \quad (4)$$

Replacing the oxygen as an electron acceptor, as in conventional PEM fuel cell The basics of the BioGenerator is shown in Fig. 1. It can be seen that iron ions are continuously shuttled between the electrochemical cell cathode (where they are reduced) and the bioreactor (where they are re-oxidized/regenerated by microorganisms). Therefore, the only input into the BioGenerator system is hydrogen fuel, oxygen as an oxidant and CO_2 as a carbon source for the microorganisms. The outputs include water, electricity, heat, and eventually excess microbial mass that is formed in the bioreactor in the course of operation. The microorganisms, growth medium nutrients and iron salts remain in the system.

The net reaction used by iron-oxidizing autotrophic microorganisms to obtain biological energy is: