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Electrochemical Energy Harvesting for IoT Applications: Comparing Electrode Materials in Galvanic Cell

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Abstract—A novel energy harvesting platform based on electrochemical energy was developed and tested in this article. The electrochemical platform consists of harvesting module, energy management electronics, supercapacitor as an energy storage, sensors, wireless data transfer and receiver. The energy harvesting module consists of two metal electrodes immersed into an electrolyte. Seawater, salt water, and salt water with a mixture of soil were used as this electrolyte medium. The mixture is a novel idea for energy harvesting for IoT. The energy obtained from the harvester platform was used to run the energy management electronics, measure temperature, humidity, air pressure and the voltage of the energy storage supercapacitor. The measurement data was sent wirelessly with Bluetooth technology to the data receiver. Results indicate that it is possible to get enough energy from the electrochemical harvester to run the whole harvesting platform with sensors and wireless data transfer. This is very advantageous because these platforms typically need batteries or connection to power grid. The suggested platform provides thus possibility for autonomous operation with reduced maintenance.

Keywords—*electrochemical; autonomous; seawater; IoT; Bluetooth, sensors*

I. INTRODUCTION

One possibility to get clean and environmentally friendly electrical energy is collecting it automatically from the surrounding environment. This collected energy can be used to power a wide range of electronics and measurement devices used by both industry and public. Energy can be harvested through various physical and chemical phenomena like electromagnetic fields, mechanical movement and vibration, electrochemical phenomena, temperature differences and friction.

Energy harvesting provides independence from batteries and mains power. Replacing the batteries is an environmentally friendly option: billions of environmentally hazardous batteries are used annually, and their recycling is difficult. Using mains power requires electric grid to be available, as well as electric wires and electronics that are suitable for mains power. Utilizing energy harvesting reduces the need for electric wires and it can be used in places without access to an electric grid. It

can thus reduce the materials needed as well as maintenance work. In this work, we develop an energy harvesting method utilizing an electrochemical phenomenon. The selected technology is called electrochemical or galvanic cells. A cell consists of three distinct parts: an anode, a cathode and an electrolyte. The oxidation reaction takes place in the anode and reduction in the cathode. The electrolyte is a substance which allows an ion flow between electrodes (the anode and the cathode).

Electric potential difference occurs between the metal electrodes and a conducting solution (electrolyte) when the electrodes are put into the solution. The solution consists of electrolyte (e.g. salt or HCl) and solvent (e.g. water). The potential difference is due to different energy levels of the electrode materials and causes charge transfer.

The electrolyte and electrode materials determine what kind of ions can be available for the electrochemical process. The reactions on the surfaces of the electrodes are due to their electrochemical properties. Electrochemical properties are described as electro-potential series (or galvanic series) in which metals are arranged based on their standard electrode potential (nobility).

In this work low alloyed structural steel and zinc plates were used as anodes and gold sheets as a cathode. Electrodes (anode and cathode) have charged surface due to which they attract oppositely charged ions (as well as dipoles). This creates a double layer or an interfacial region at the contact boundary between an electrode surface and electrolyte [1]. This double layer reduces the current flow in the electro chemical cell. The double layer is mainly on electrolyte. Even though the layer is very thin (nanometers), many phenomena are related to it, for example: energy barrier, electron transfer, DC potential and electrode [1]

In our tests, seawater (NaCl concentration 0,07 %), salt water (NaCl concentration 3 %) as well as salt water (NaCl concentration 3 %) mixed with soil was used. In seawater there are several other ions like chloride (Cl⁻), sodium (Na⁺), sulfate (SO₄⁻), magnesium (Mg²⁺), calcium (Ca²⁺), and potassium (K⁺). All these ions provide specific conductivity due to ion motion. The electric conductivity depends on the concentration

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of the ions. The goal is to compare electrode pairs: Steel-Gold and Zinc-Gold with these three different electrolyte solutions. The mixture of salt water and soil is a novel solution which is not utilized before for IoT energy harvesting.

Seawater has been already utilized in different power generation applications like hydrogen production. A reverse electro dialysis approach is introduced to capture the salinity gradient energy (SGE, salinity gradient energy harvesting) between the concentrated seawater and seawater for power production: Li et al. researched the concentrated seawater discharged from desalination plants [2]. This water has high salinity and temperature, and the direct discharge deteriorates offshore ecology as well as wastes energy. The feasibility of this approach is verified by experimental and simulation studies on a RED stack.

Jwa et al. 2022 utilized this for on-site disinfection of natural seawater [3]. Seawater batteries (SWBs) have also been studied and developed by several researched. Park et al. 2020 utilized Na ion from seawater as a cathode material and solid carbon as anode with high surface area [4]. The power performance was 16.2 mW/cm^2 . Ha et al uses two carbon materials with distinct surface potentials as electrodes [5]. The ion-redistribution between electrodes enables continuous self-charging. This electricity generator reached an open circuit voltage of $\sim 300 \text{ mV}$ and a power density of 24.60 mW cm^{-3} .

II. EXPERIMENTAL SET-UP

The experimental arrangements of the electrochemical energy harvesting and measuring method are shown in Fig. 1 as a block diagram. The measuring arrangements consist of the energy harvester platform and separate Arduino Nano IoT based monitoring circuit. The basic setup of the harvester platform consists of a) electrochemical module, with electrodes (e.g. Zn and Au) and electrolyte seawater and soil+water+NaCl, b) energy management electronics and energy storage, c) measuring sensor unit connected with a Bluetooth Low Energy (BLE) data transmitter which broadcasts the measurement data to the external computer gateway. d) computer working at a gateway and e) ThingsBoard Cloud.

The sensor unit measures temperature, humidity and air pressure. Bluetooth transmitter sends the measured data wirelessly to the battery powered Raspberry Pi gateway. The separate Arduino Nano IoT measurement circuit was used to monitor the functioning of the energy harvester platform. This monitor circuit measured electrode cell voltage and voltage of the energy storage supercapacitor. The monitoring circuit is battery powered. The data collected through the monitoring circuit and the BLE device was received via BLE by the gateway unit and transmitted to the ThingsBoard cloud. The measurement data could be visualized on the ThingsBoard cloud dashboard.

The efficiency of the whole system is planned to be measured in the future research. The main goal was to first build a platform which can operate autonomously i.e. without batteries or connection to power grid. The developed system achieved this goal; battery is used only gateway and power grid

in cloud dashboard and devices used for measuring the unit itself.

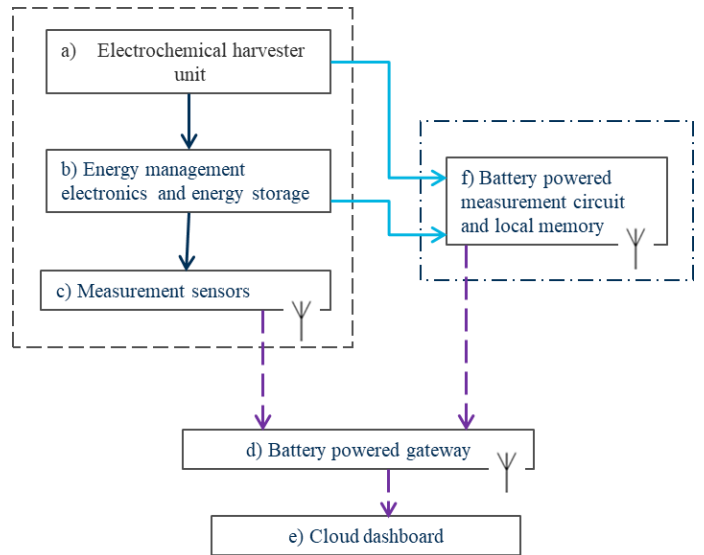


Figure 1. Block diagram of energy harvesting platform. a) electrochemical harvester unit, b) energy management electronics and energy storage, c) measuring sensor unit connected with a Bluetooth Low Energy (BLE) data transmitter, d) computer gateway, e) ThingsBoard Cloud, f) separate battery powered measurement circuit and local memory.

Energy harvesting and management electronic circuit is shown on Fig. 2. The circuit was planned in the electronics laboratory in Vaasa University. The circuit is based on the use of National Instruments circuit model no. BQ2.

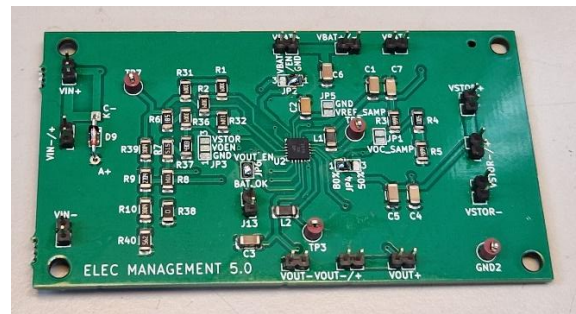


Figure 2. Energy harvesting and management circuit.

To monitor the voltage levels in the energy harvesting circuit, we used microcontroller-based measurement circuit. The measurement circuit utilizes a voltage divider and analog-to-digital converter to measure voltages. The equation to calculate the voltage with voltage divider is shown in Eq. (1), where V_{in} is the input voltage, V_{out} is the voltage measured by analog-to-digital converter, and R_1 and R_2 are the resistors in the voltage divider. The separate measurement circuit is not powering the energy harvesting platform.

$$V_{in} = V_{out} \cdot \left(1 + \frac{R_1}{R_2}\right) \quad (1)$$

Fig. 3 shows the electrochemical harvester module: Au-Zn and Au-Fe were used as electrodes. Au was a cathode and Zn and Fe were anode. The size of the electrodes was 60 x 100 mm. Electrode cell was placed in a 500 ml glass beaker. As electrolyte seawater (NaCl concentration 0.07 %), salt water NaCl concentration 3 %), and a mixture of saltwater (NaCl concentration 3%) and soil (250 g) were used in the measurements.

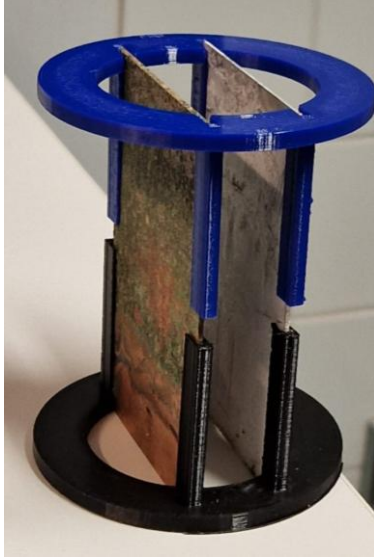


Figure 3. Electrochemical harvester unit with electrodes. Size of the plates 60 x 100 mm.

III. RESULTS

One of the ways to compare different electrolytes as well as different electrode pairs (Zinc-Gold and Steel-Gold) is the voltage output from the electrochemical reaction inducted. This voltage is stored in the supercapacitor of the platform, measured and its value is sent to the cloud. Figure 4 shows a typical shape of voltage curve obtained from these voltage measurements.

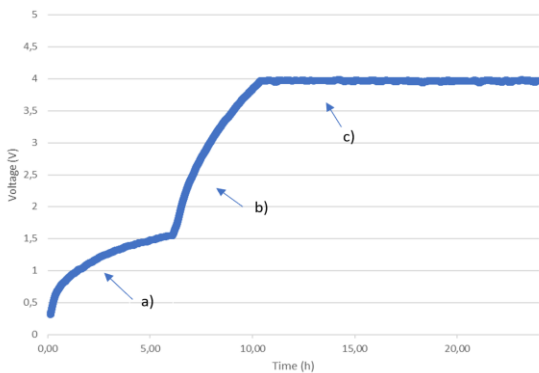


Figure 4. Voltage of the energy storage supercapacitor, electrode Au and Zn, a mixture of seawater and soil as an electrolyte (0.07 %) a) starting cycle, b) recharge cycle and c) operating cycle.

The curve shows a knee point which is due to the operation principle of the platform. In the beginning of the measurement the voltage of the supercapacitor was set to 0 V. As Figure 4 shows, the voltage of the initially empty supercapacitor increases up to 4 V during about 10 h. The knee point in the curve (Fig. 4(a.)) with a voltage value of about 1.5V is because of the energy management electronic circuit charges smaller capacitors first to work properly. After 1,5 V the circuit starts to load only the super capacitor, which will boost the charging process. When reaching the value of 4 V the measurement sensor unit starts to work, and the integrated Bluetooth wireless data transmitter unit starts to send the data wirelessly to the battery powered gateway (d) in Fig 1. The gateway sends the collected data to the Cloud Dashboard where it can be read by a computer connected to the network. The energy accumulated to the supercapacitor with the electrochemical reaction is enough to keep the voltage of the supercapacitor in 4 V. Also, in the supercapacitor there is enough energy for the continuous powering of the measurement sensor unit and the Bluetooth transmitter sending the data to the Cloud Dashboard.

It is well known that higher salt concentration (NaCl) will increase ionic conductivity up to saturation. Therefore, we made a salt and water mixture with 3 % salt concentration. This is lower than the average seawater concentration of 3.5 % [6]. Figures 5-6 show charging voltage of the energy storage supercapacitor as a function of time for the NaCl electrolyte with Zinc-Gold, and Steel-Gold electrode pairs, respectively. The electrochemical system was subjected to multiple successive charge-discharge cycles. The system was not disturbed during the cycles, i.e. it was not stirred or liquid added. Figures 5-6 shows only results for selected times – after several cycles, time to reach the maximum voltage (around 4.5 V) increases. For Zinc-Gold electrode pair experiment, the rising time increased from around 4 minutes at the beginning to approximately 10 minutes after 96 hours.

The increase in rising time may indicate the formation of the double layer. The electrochemical system with Zinc-Gold electrodes has a shorter time to reach full voltage of 4.5 V. However, the autonomous operation of the implemented platform is possible in both cases.

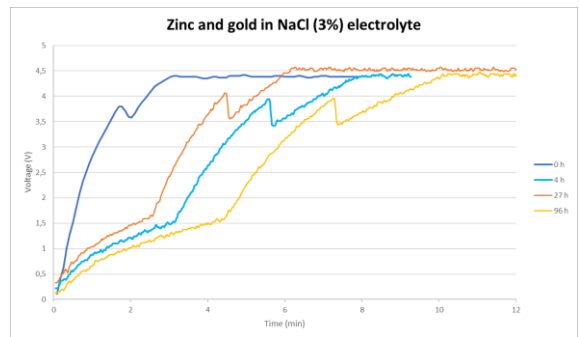


Figure 5. The charging voltage of the supercapacitor as a function of time when Zinc-Gold electrode pair with water and NaCl 3 % electrolyte was used.

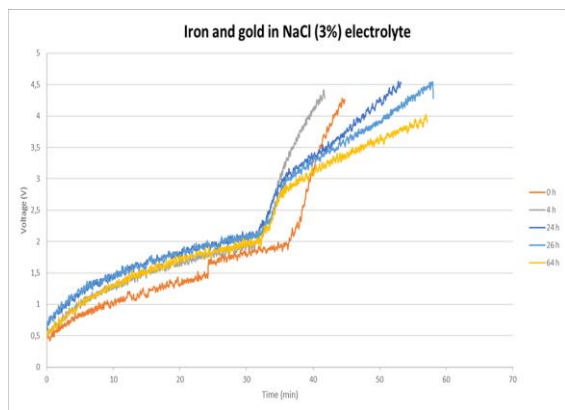


Figure 6. The charging voltage of the supercapacitor as a function of time when Steel-Gold electrode pair with water and NaCl 3 % electrolyte was used.

The difference in electrode activities between Steel-Gold and Zinc-Gold electrode pair might be at least partially due to the difference in electrochemical potentials. For example, the web page of Electrochemical potentials (<https://www.qsl.net/n9zia/electrochemical.html>, adapted from RF connector guide <https://www.k3emd.com/downloads/RFConnectorGuide.pdf>) in 2 % salt water, gives the electrochemical potential between Gold-Stainless Steel pair as 110 mV whereas the potential for Gold-Zinc pair is given as 1270 mV. This indicates higher potential differences between Gold and Zinc and thus may cause higher charging speed. Even though gold is expensive, it is not consumed in the reaction and the amount needed is small as the electrode was just gold-plated.

In Figure 7, the soil (250 g)-water (3 % NaCl) electrolyte is used for testing. Adding soil provides more ions, thus improving the performance of electrochemical cells. The more ions are available, the better the conductivity. This means that the charging time is shorter than with only salt-water

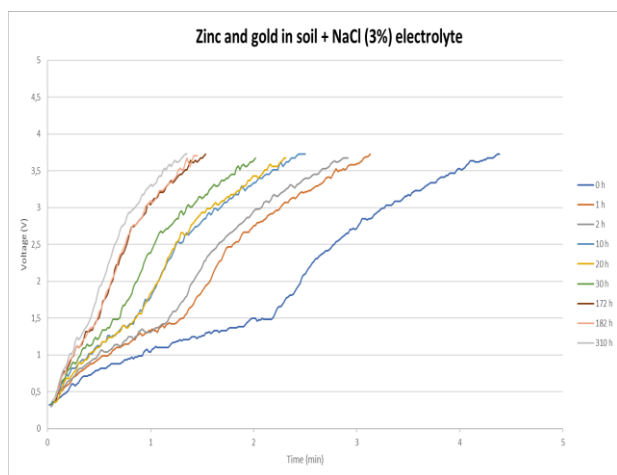


Figure 7. Supercapacitor voltage as a function of time for Zinc-Gold electrodes and soil-water (3 % NaCl) electrolyte.

Voltage information alone does not give a full picture of the operation of the electrochemical system. The current level must

also be considered for system design. Higher values for both current and voltage levels are naturally wanted. This can be described as power which describes here the amount of energy transferred from the electrochemical reaction to the platform. Power is obtained by multiplying current and voltage values.

Figures 8 and 9 show the power as a function of time for both electrode pairs. For Zinc-Gold pair the power is higher and increases over 400 microwatts in later cycles. Steel-Gold pair produces a maximum value (around 25 microwatts) in the first cycle and after that, the power value decreases. This indicates that Zinc-Gold pair has more durability as well as produces more power than Steel-Gold pair.

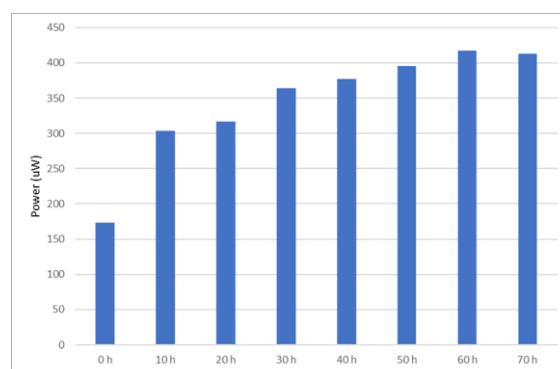


Figure 8. Average supercapacitor charging power. Zinc and gold electrodes in soil (250 g)-water (3 % or 7.5 g NaCl, tap water 246 g) electrolyte.

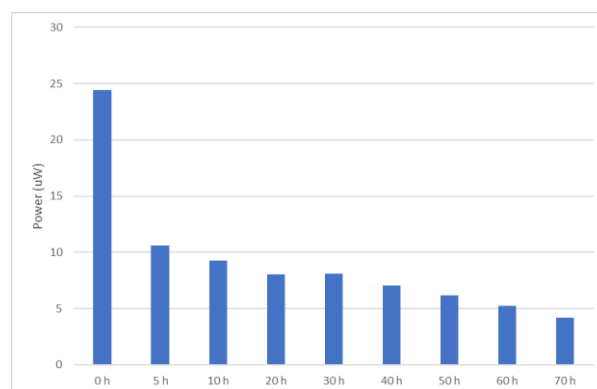


Figure 9. Average supercapacitor charging power. Steel and gold electrodes in soil (250 g)-water (3 % or 7.5 g NaCl, tap water 250 g) electrolyte.

IV. CONCLUSIONS

In this paper, we demonstrated that a novel IoT platform with electrochemical harvester could work autonomously. The electrochemical harvester was tested with three different solutions and two electrode pairs. First, we used seawater from Baltic Sea with low salt concentrations. This test indicated that even in low concentration, the harvester was capable of operating. Then we tested with salt water with 3 % salt concentration for two different electrode pairs (Zinc-Gold and

Steel-Gold). Both electrode pairs provided enough energy for several cycles over a three-day period. When comparing power output from electrode pairs, the Zinc-Gold pair provided higher values. Last, we tested the Zinc-Gold pair with a mixture of salt water and soil as an electrolyte. This is a novel choice for an electrolyte. It was also the option as it provided shorter charging time than plain salt water.

V. ACKNOWLEDGEMENT

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