

Impedance Spectroscopy Analysis of a Thermo-electrochemical Cell Under Operating Conditions

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Abstract— Low-grade (<200 °C) heat is an abundant and available energy not generally exploited. In this regard, the so-called thermo-electrochemical cells have become a valid opportunity to harvest this ubiquitous source of heat. They are capable to convert heat into electricity by means of the temperature-redox potential dependency of a redox couple. In fact, they present Seebeck coefficient values in order of mV/K, much higher than solid-state thermoelectrics. In this work, a system formed by two Pt electrodes in contact with a 0.4 M ferro/ferricyanide aqueous solution has been studied by means of impedance spectroscopy under operating conditions ($\Delta T=40$ K). The main processes which govern the performance of the system have been identified, which lead to different resistances: (i) electrolyte ionic resistance, (ii) charge transfer resistance and (iii) mass transfer resistance. It was also demonstrated that the current-voltage characteristics of the device can be obtained knowing the open-circuit potential and performing a single impedance spectroscopy measurement, which determines the device dc resistance. This method can save a significant amount of time in many cases.

Keywords— Thermocells, thermogalvanic cells, liquid thermoelectrics, redox species.

I. INTRODUCTION

More than 60% of the total world energy is lost as waste heat. To take advantage of this ubiquitous source of energy, thermoelectric (TE) devices can directly convert heat into electricity under safe, clean, and environmentally friendly operation [1]. A good TE material should have a high Seebeck coefficient (S) and electrical conductivity (σ), but a low thermal conductivity (κ). To date, most of TE materials are inorganic solids, typically exhibiting low S values (200-250 μ V/K), so low-temperature heat harvesting is still challenging [2]. In the last decades, thermo-electrochemical cells (or thermocells TCs or thermogalvanic cells) have gained attention as a suitable option for heat-to-electricity conversion at low temperatures (<200 °C). They can provide Seebeck coefficient values in order of mV/K, almost three orders of magnitude higher than usual solid-state thermoelectrics. The origin of this higher Seebeck coefficient is the redox potential-temperature dependence of the redox species in the electrolyte. Despite this advantage, device resistance values are much higher than in solid-state TEs, and consequently efficiencies are quite low. This is the main limitation of TCs, since thermal conductivities of electrolytes are typically low (<1 $\text{Wm}^{-1}\text{K}^{-1}$). Among all the TC systems currently present, the one formed by two Pt electrodes separated by an aqueous solution of 0.4 M $\text{K}_3(\text{FeCN}_6)/\text{K}_4(\text{FeCN}_6)$ is the benchmark system in the literature. This device shows a high S (≈ 1.4 mV/K) and high kinetics parameters that lead to relatively large power outputs when the system is connected to an external load [3].

In order to obtain the total device resistance ($R_{I,V}$) and the power output, a current-voltage I - V curve is typically performed under steady state conditions. Waiting for these

conditions at each point of the I - V curve can many times take a significant amount of time due to the slow diffusion rate of the redox species present in the electrolyte solution [4]. We present here a way to more easily obtain the I - V curve of a TC, which requires the knowledge of the open-circuit potential and an impedance spectroscopy (IS) measurement at this voltage. The article shows first the experimental part. Then, explains the typical equivalent circuit of a TC, and finally analyses the method to obtain the I - V curve.

II. EXPERIMENTAL PART

A custom setup was built to characterise a fabricated TC under operating conditions (see Fig. 1). The TC consisted of two Pt electrodes (0.1 mm thickness and 1 cm x 1 cm area from Glentham, ref. GX2917) (see Fig. 1a). These pieces were cleaned before using them by means of two sonication steps of 15 min in different media. In the first step, sonication was carried out in distilled water to remove possible impurities. Finally, isopropanol (Labkem, ref. PROL-POP-5K0) was employed for sonication. A solution of 0.4 M potassium ferrocyanide (Sigma Aldrich, ref. P3289-100G) and 0.4 M potassium ferricyanide (Fluka, ref. BCBT1564) in milli-Q water was employed as the electrolyte. All the chemicals were used as received.

In order to establish a temperature difference in the setup, two copper blocks were employed. One of them, with 30 mm x 30 mm x 10 mm dimensions and 2 cartridge heaters inserted (Watlow, ref. C1A-9604), acted as the heat source. A second larger copper block (40 mm x 40 mm x 10 mm) with a water circulation channel was used as the heat sink (see Fig. 1b). A water circulator (PolyScience, ref. SD07R-20-A12E) was employed to circulate the water and control the temperature of the Cu block.

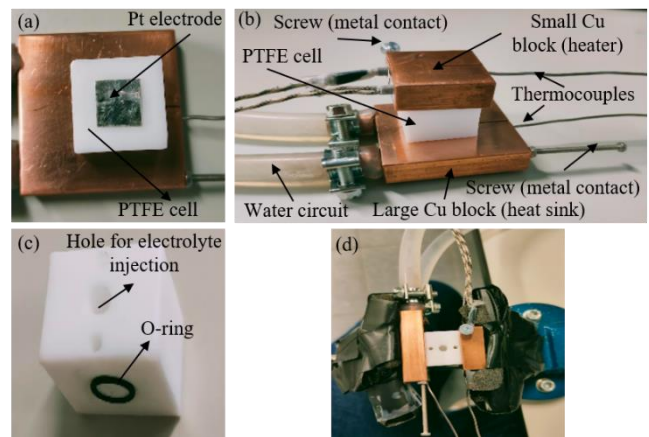


Fig. 1. Photographs of (a) a Pt electrode on top of the PTFE cell with the O-ring, (b) the PTFE cell with the O-ring, (c) the setup mounted but not clamped, and (d) the setup clamped.

The Pt electrodes were placed centered on top of the copper blocks, which are separated by a

polytetrafluoroethylene (PTFE) cell which contains the electrolyte in a circular channel. The separation of the electrodes d was 14 mm. The channel is connected to a top hole for the injection of the electrolyte (see Fig. 1c).

To avoid leaks during the experiments, two O-rings were used pressing each of the electrodes (see Fig. 1c). The area of the O-ring, which determines the area of the electrodes in contact with the electrolyte was $A=0.5 \text{ cm}^2$. A very little amount of thermal grease (RS, ref. 2173835) was put covering only part of the Pt/Cu interfaces to improve the thermal contacts. To contact the device, two screws were screwed in the Cu blocks, which served as metal contacts (see Fig. 1b). The screws were connected to the apparatuses by crocodile connectors. Once all the elements were mounted, the setup was clamped using pieces of foam at the clamping points to reduce heat losses (see Fig. 1d).

The Seebeck coefficient, which indicates the variation of the open-circuit potential (V_{oc}) with the temperature difference (ΔT) was obtained from the slope of a V_{oc} vs ΔT plot. For all the points the cold side temperature was kept constant at $21.5 \pm 0.2 \text{ }^\circ\text{C}$. The V_{oc} was measured with a Keithley 2100 nanovoltmeter, and the temperature difference was varied in steps of $\approx 10 \text{ K}$, from 0 up to $\approx 40 \text{ K}$, by powering the two cartridge heaters inserted in the small Cu block by means of a Keithley 2601 sourcemeter. Two K-type thermocouples (RS, ref. 8140134) and a dual thermometer (RS, ref. 1316) were used to monitor the hot and cold side temperatures. Both thermocouples were inserted in holes performed at the Cu blocks. An I - V curve measurement was performed at $\Delta T=40 \text{ K}$ ($T_{cold}=21.5 \text{ }^\circ\text{C}$) by fixing different voltage values and recording the corresponding current after steady state is reached. An IS measurement was carried out at the open-circuit potential when the cell was at $\Delta T=40 \text{ K}$ ($T_{cold}=21.5 \text{ }^\circ\text{C}$). An amplitude of 15 mV and the 100 kHz-3 mHz frequency range was employed. The I - V and IS measurements were performed using a Vionic potentiostat from Metrohm Autolab, controlled by Intello 1.3.2 software.

III. RESULTS AND DISCUSSION

Fig. 2 shows the V_{oc} - ΔT plot of the fabricated TC. It can be observed that the experimental points perfectly fit to a straight line of $1.35 \pm 0.01 \text{ mV/K}$ slope value, which is the Seebeck coefficient of the device. This value is very similar to the one typically reported in the literature (1.4 mV/K) [3].

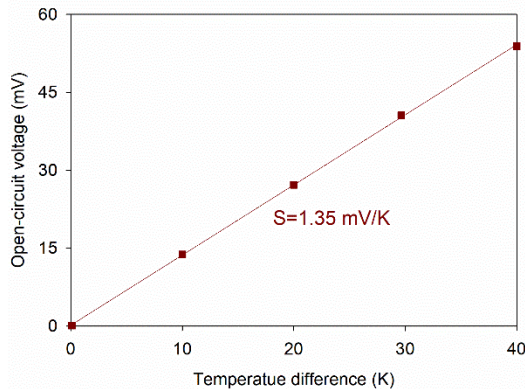


Fig. 2. Open-circuit vs temperature difference plot. The line represents the fitting to a straight line. The slope provides the Seebeck coefficient (S).

IS measurements were performed to the TC. Before their analysis, we would like to remark that IS is a method that

allows to identify and separate the different processes that occur in a device. Impedance results are typically analysed by means of equivalent circuits. Each element of the equivalent circuit describes one of the processes. One of the most well-known equivalent circuits is the Randles circuit [5], which can serve as the basis to analyse the impedance response in a TC. Fig. 3 shows the Randles circuit (inset) and its typical Nyquist plot.

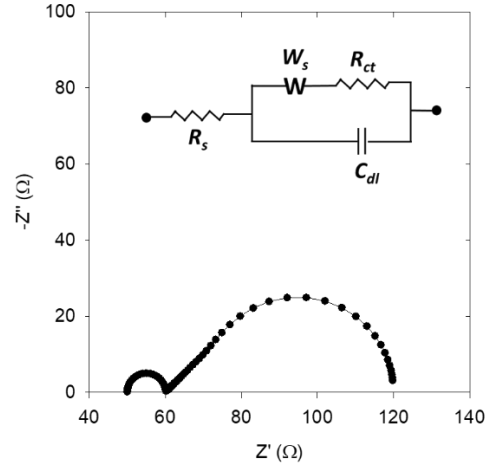


Fig. 3. Nyquist plot of a Randles circuit (in the inset) obtained using $R_s=50 \text{ } \Omega$, $R_{ct}=10 \text{ } \Omega$, $W_r=60 \text{ } \Omega$, $W_i=25 \text{ s}$, $W_p=0.5$ and $C_{dl}=1 \text{ } \mu\text{F}$.

The intercept with the Z' axis at the left part ($50 \text{ } \Omega$) is the resistance of the electrolyte solution (R_s). The semicircle at the left is the parallel combination of the charge transfer resistance (R_{ct}) and the capacitance of the electrical double layer (C_{dl}). It should be noted that these two elements might not be observed when Pt electrodes are used, due to the catalytic effect of this metal, which highly reduces R_{ct} . The 45° line overlapped with a semicircle after the previous semicircle relates to the diffusion of redox species from the Pt/electrolyte interfaces towards the bulk of the solution. This process is represented by the Warburg shorted element (W_s). This element contains the mass transfer resistance (R_{mt}) associated with the transport of redox species from the Pt/electrolyte interfaces to the bulk of the solution.

The IS results of the TC can be seen in Fig. 4. It can be observed that the spectrum can be fitted with a Randles circuit where the charge transfer process occurs very quickly (R_{ct} and C_{dl} do not appear, see inset of Fig. 4), as expected by the use of Pt as electrodes.

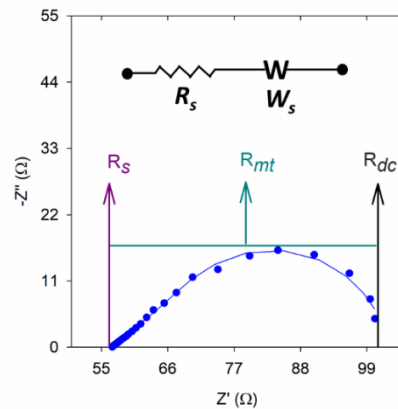


Fig. 4. Impedance spectrum of the thermocell under a temperature difference of 40 K ($T_{cold}=21.5 \text{ }^\circ\text{C}$). The line is the fitting to the equivalent circuit of the inset. The graphical determination of R_s , R_{mt} and R_{dc} is also indicated.

From the fitting, the values of R_s , R_{mt} and R_{dc} can be obtained (see Table I), being R_{dc} the impedance value when frequency tends to zero (steady state). In this TC, $R_{dc}=R_{\Omega}+R_{mt}$. The values of these resistances can also be estimated graphically, as indicated in Fig. 4. It should be noted that the Warburg element of the equivalent circuit might not be exactly the Warburg element of a Randles circuit, since the diffusion coefficients of the redox species might be affected by the temperature gradient in the device and other processes such as convection in the electrolyte could take place.

Table 1. Different parameters obtained and calculated from the impedance and I - V curve measurements. Values between brackets indicate relative errors from the fitting.

R_s (Ω)	R_{mt} (Ω)	R_{dc} (Ω)	R_{I-V} (Ω)	ϵ_R (%)	η (%)	η_C (%)
56.8 (0.13)	45.8 (0.75%)	102.6	106.7	3.84	0.0096	0.08

In addition to the IS measurement, the I - V curve of the TC at the same condition ($\Delta T=40$ K) was obtained (see Fig. 5). A linear correlation was observed for the current and the voltage. The slope of this correlation, $R_{I-V}=106.7 \Omega$, represents the total device resistance. It can be observed that R_{I-V} matches well with the R_{dc} value obtained from the IS results. The deviation between them ϵ_R is just 3.84% (see Table I). This fact allows the determination of the I - V curve just by knowing the V_{oc} at the given temperature difference and by extracting R_{dc} from an IS measurement at this voltage, which can simplify significantly the experimental determination of the I - V curve, usually carried out fixing different load resistances (or voltages) and waiting for steady state to be reached, which ends up being a lengthy process in many cases.

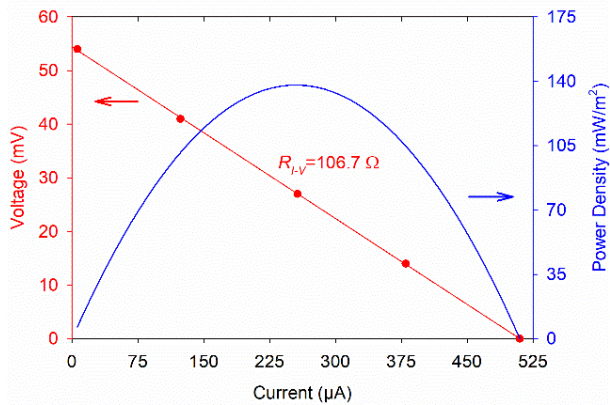


Fig. 5. Current-voltage and power output density curves at $\Delta T=40$ K ($T_{cold}=21.5$ °C). The red line represents the fitting to a straight line, whose slope value is R_{I-V} .

In addition, the IS measurement makes possible to determine the contributions to the total device resistance,

which in this case come from R_s and R_{mt} , contributing both nearly equal (see Table I).

Finally, we would like to remark that the maximum power output density obtained from the TC was $P_{max}=138$ mW/m², in the same order of magnitude than the values reported in the literature [3]. The efficiency η and the Carnott efficiency η_C , calculated by means of the equations $\eta=V_{oc}I_{sc}/(4\kappa A\Delta T/d)$ and $\eta_C=\eta/(\Delta T/T_{hot})$, respectively, being $I_{sc}=I(V=0)$, κ the thermal conductivity of the electrolyte (0.5 Wm⁻¹K⁻¹ for our electrolyte [6]), and T_{hot} the hot side temperature, were also calculated and in agreement with the literature [3].

IV. CONCLUSIONS

We have analysed the impedance spectroscopy results under operating conditions of a standard thermocell fabricated with Pt electrodes and 0.4 M ferro/ferricyanide aqueous electrolyte. A simplified Randles equivalent circuit was used to fit the impedance response at the open-circuit voltage value of the thermocell under a temperature difference of 40 K. From the fitting, the resistance at steady state R_{dc} was calculated as the addition of the charge transfer R_s and mass transport R_{mt} resistances ($R_{dc}=R_s+R_{mt}$). It was found that the device resistance, obtained from the current-voltage curve, matches well with R_{dc} . Hence, knowing R_{dc} and the open-circuit voltage V_{oc} at the given temperature difference, the current-voltage curve can be determined, as well as the power output, which can reduce a significant amount of time in many cases.

ACKNOWLEDGMENTS

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 863222 (UncorrelaTEd project). Mauricio Solis-de la Fuente and Lourdes Márquez-García are also acknowledged for their technical support.

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