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The amplifying effect of natural convection on power generation of thermogalvanic cells

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ABSTRACT

Recent development of new electrolytes and electrode materials has shifted the research focus away from other routes to improved thermogalvanic cells, also known as thermocells or thermoelectrochemical cells. A thermogalvanic cell can be designed to achieve a relatively high maximum power output (P_{max}) if convection is incorporated within the cell. Here we show through experimentation and modeling that natural convection is not a hindrance, but a plausible aid to improve power generation of thermogalvanic generators. The natural convection conditions are varied via orientation of the cell and electrode spacing. Experimental testing revealed an optimum concentration of 0.7 M $CuSO_4$ aqueous electrolyte, with the addition of 0.1 M H_2SO_4 as background electrolyte, results in P_{max} improvements of up to 100%, from ~0.8 to ~1.6 μW cm^{-2}, in a horizontal cell operating between the vertical cold and hot copper (Cu) electrode temperatures of 5 and 65 °C, respectively. The experimental data reported here compare well with those from the few previously reported studies of Cu/Cu^{2+} cells. However, comparison with the conventional $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ cells revealed a completely different dependence of the electrode spacing on the power generation, that the P_{max} of Cu/Cu^{2+} cell increases, instead of decreases, with the electrode spacing due to the difference in ionic transfer mechanism. Herein, we also develop a simple expression which predicts the ratio between the P_{max} of a thermogalvanic generator with and without convection in terms of Sherwood, Nusselt, and Lewis numbers. The predictions are in reasonable agreement with our experimental data; both show that convection is primarily responsible for the enhancement in P_{max} of thermogalvanic generators.

1. Introduction

Thermogalvanic cells, which are also referred to as "thermoelectrochemical cells" or simply as "thermocells", have been studied since 1825 [1]. In the past two decades [2] research on them has been motivated by their potential to convert low-grade thermal energy to electricity. One of the earliest experiments [1] was carried out using a cell with copper (Cu) electrodes immersed in a $CuSO_4$ aqueous solution (Fig. 1). The temperature difference (ΔT) between the cold and the hot electrodes creates a difference in electrochemical potential equilibrium of the redox couple on the electrodes. If the electrodes are connected to a load, this potential difference drives the oxidation of Cu on the cold electrode (anode) [2]:

$$Cu \rightarrow Cu^{2+} + 2e^-$$

and the reduction of Cu^{2+} cations on the hot electrode (cathode):

$$Cu^{2+} + 2e^- \rightarrow Cu$$

so that electrical current and power can be delivered, thus converting thermal energy into electrical energy. Thermogalvanic cells have long been known in the electrochemistry community, but have not received much attention from the thermal transport community. This is surprising given that their performance is highly dependent on controlling both thermal and mass (ionic) transport.

Earlier approaches to increase the Seebeck coefficient, power output (P), and the efficiency (η) of thermogalvanic generators

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Nomenclature

A	geometric reactive area of the electrode (m^2)
C	concentration (mol m^{-3})
c_p	constant pressure specific heat (J kg^{-1} K^{-1})
D_{AB}	mass diffusivity of species A in mixture B (m^2 s^{-1})
E	potential difference (V)
F	Faraday constant (A s mol^{-1})
g	gravitational acceleration (m s^{-2})
Gr	Grashof number
H	electrode diameter (m)
I	current (A)
j	current density (A m^{-2})
j_l	limiting current density (A m^{-2})
k	thermal conductivity (W m^{-1} K^{-1})
L	inter-electrode spacing (m)
L_c	characteristic length (m)
Le	Lewis number
n	number of electrons involved in reaction
Nu	Nusselt number
P	power output (W)
Pr	Prandtl number
$\dot{q}$	heat flux (W m^{-2})
R	resistance (Ω)
Sc	Schmidt number
Sh	Sherwood number
T	temperature (K)

Greek symbols

α	thermal diffusivity (m^2 s^{-1})
γ	factor, Eq. (9)
δ	boundary layer thickness (m)
Δ	change
η	power conversion efficiency
μ	dynamic viscosity (kg m^{-1} s^{-1})
ν	kinematic viscosity (m^2 s^{-1})
ρ	density (kg m^{-3})
σ	electrical (ionic) conductivity (Ω^{-1} m^{-1})

Subscripts

∞	of bulk electrolyte
a,o	at the anode's surface
avg	average
c	cold
C	solutal
c,o	at the cathode's surface
cond	conductive
conv	convective
ext	external
h	hot
int	internal
max	maximum
mp	at maximum power output
o	at the electrode's surface
oc	open-circuit
r	relative to that of a Carnot engine operating between the same temperatures
T	thermal
Ω	ohmic

were dedicated to exploring new electrolytes and electrode materials [3,4]. Our recent review article [2] showed the same trend. We revealed that the highest Seebeck coefficient of 7.16 mV K^{-1} was reached by Bonetti et al. [5] for a cell with tetrabutylammonium in dodecanol electrolyte and platinum (Pt) electrodes. The highest maximum power output, a P_{max} of 1.8 W m^{-2} corresponding to a power conversion efficiency relative to that of a Carnot engine operating between the same temperatures, $\eta_r = \eta/(1 - T_{cold}/T_{hot}) = 1.4\%$, was achieved by Hu et al. [6] with carbon-multiwalled nanotubes buckypaper electrodes in a ferro/ferricyanide ($Fe(CN)_6^{4-}$/$Fe(CN)_6^{3-}$) aqueous electrolyte. Motivated by these results, Im et al. [7] recently demonstrated that $Fe(CN)_6^{4-}$/$Fe(CN)_6^{3-}$ thermogalvanic cell can be embedded on a T-shirt and is flexible enough to optimally harness the heat from human body and store the power into a capacitor for later use. Additionally, Lee et al. [8] showed that Cu/Cu^{2+} thermogalvanic cell offers a great potential application in thermally regenerative electrochemical cycle (TREC) as an alternative to utilize low-grade heat sources. Abraham et al. [9,10], Zinovyeva et al. [11], and Jiao et al. [12] more recently reported new experimental data for ionic liquid thermogalvanic cells, while Manda et al. [13] and Abraham et al. [14] used activated charcoal and catalytically active poly(3,4-ethylenedioxythiophene), PEDOT, –deposited electrodes, respectively. Due to the fact that advanced electrolyte and electrode materials represent a clear path to high performance, geometry and operational characteristics of the cell have been largely overlooked as an improvement route. In particular, we argue here that design configurations which utilize natural convection are a viable way to increase energy transfer within the cell.

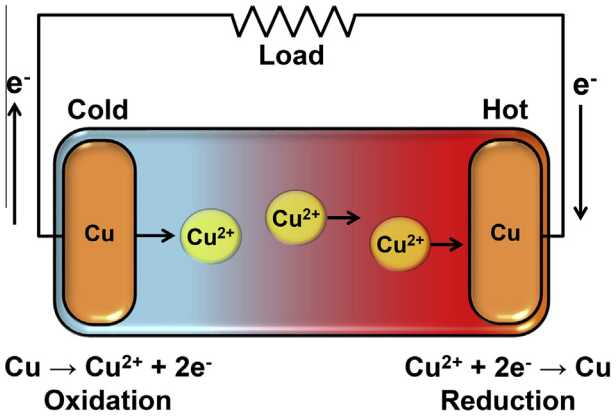

Fig. 1. Schematic of $Cu|Cu/Cu^{2+}, H_2O|Cu$ thermogalvanic cell.

Forced convection using rotating electrodes [15], pumps or flow cells [16], and the application of external current onto the electrodes (to generate concentration difference) [15,17–21] to enhance convection have also been investigated by various researchers. However, these external power consumptions can be parasitic and may lead to an unfair comparison in terms of power conversion efficiency between thermogalvanic devices when energy audits are to be carried out [4,22]. Additionally, such systems have limited practical appeal since they require moving parts to convert heat into electricity.

The aim of this study is to demonstrate that, in general, thermogalvanic power generation can be enhanced by designing an optimum cell geometry that controls and utilizes natural convection, without external forces of any kind, to increase energy and mass transfer within the cell. This study will also try to present a simple theoretical treatment aimed to provide future researchers and engineers with a useful preliminary design metric for constructing the optimum cell architecture. Before looking at our results to see