



Short communication

## Combining thermogalvanic corrosion and thermogalvanic redox couples for improved electrochemical waste heat harvesting



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## ABSTRACT

Thermogalvanic (or thermoelectrochemical) systems can convert a temperature difference into an electrical current by exploiting the entropy change associated with a redox process. This work investigates coupling thermogalvanic redox processes with thermogalvanic corrosion. Ferri/ferrocyanide and iodide/triiodide redox couples were investigated at platinum and stainless steel electrodes. Dilute iodine displays a Seebeck coefficient of  $+0.26 \text{ mV K}^{-1}$  at platinum electrodes and  $+2.1 \text{ mV K}^{-1}$  at stainless steel electrodes. An apparent Seebeck coefficient of  $+13.6 \text{ mV K}^{-1}$  could be achieved under optimal conditions. This is demonstrated to be due to a combination of the iodide/triiodide thermogalvanic redox couple and thermogalvanic iodine-induced corrosion of the stainless steel.

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## 1. Introduction

Thermogalvanic cells (or thermocells or thermoelectrochemical cells) can convert waste heat into an electrical current [1–3]. Principally, such assemblies require two electrodes that are at different temperatures, in contact with a common (solid or liquid) electrolyte and a suitable redox couple.

Ferricyanide and ferrocyanide represent a common redox couple utilised in thermogalvanic cells [4]. Reduction of ferrocyanide to ferricyanide results in a net increase in entropy [5]. In thermogalvanic cells containing a mixture of ferri- and ferrocyanide, entropy can be maximised by the conversion of ferro- to ferricyanide at the hot electrode and *vice versa* at the cold electrode; this can be achieved by electron flow from the hot electrode to the cold electrode through an external circuit. The potential difference ( $\Delta E$ ) generated across the electrodes is thus proportional to the temperature difference ( $\Delta T$ ) and the entropy change ( $\Delta S_{\text{ferri/ferro}}$ ) [6]. This relationship is characterised by the Seebeck coefficient,  $S_e$ , which for a solution of  $0.2 \text{ M K}_3[\text{FeCN}_6]$  and  $0.2 \text{ M K}_4[\text{FeCN}_6]$  is *ca.*  $-1.4 \text{ mV K}^{-1}$  [4]. The relationship between these parameters is expressed by Eq. (1) [6].

$$S_e = \frac{dV}{dT} = \frac{\Delta S_{\text{ferri/ferro}}}{nF} \quad (1)$$

Ferri/ferrocyanide is arguably the ‘benchmark’ system for aqueous solutions [1,4,7,8]. Nano-roughening a surface (*e.g.* going from platinum to platinum black) has virtually no effect [7], as the solution-phase

thermodynamics of the system are unchanged, and bulk diffusion-limited flux (on the micron scale) is essentially unchanged by nanometer scale roughening of a planar surface [9]. However, moving to 3D hierarchical nanostructures can result in enhanced flux to the electrode surface and therefore improved currents [4,8]. While such modification can boost current (extensive effect), the efficiency of heat conversion to a current is largely dependent upon intensive properties, including  $S_e$ . The simplest way to approximate the efficiency of such devices is the dimensionless  $ZT$  parameter (Eq. (2)),

$$ZT = \frac{S_e^2 T \sigma}{\kappa} \quad (2)$$

where  $Z$  is the ‘figure of merit’,  $T$  is the absolute temperature,  $\sigma$  is the ionic conductivity, and  $\kappa$  is the thermal conductivity [7]. This elegantly expresses that facile ion transfer and frustrated heat transfer benefit performance, while  $S_e$  (the entropic driving force) is the dominant factor.

Thermogalvanic systems can operate with solution-phase redox couples, with redox active electrodes (*i.e.* two copper electrodes in contact with copper sulphate solutions), or even solid-state electrolytes [1]. Thermogalvanic corrosion refers to localised corrosion occurring due to a temperature difference; the  $\text{Cu}(0) | \text{Cu}(\text{II}) | \text{Cu}(0)$  systems can be seen as thermogalvanic corrosion paired with thermogalvanic electrodeposition. Recent studies have expanded beyond aqueous systems, to investigate redox systems centred on Fe [10,11], Cr [10], Co [12], I [13], and S [14], in electrolytes such as ionic liquids [10–14] and organic solvents [12,13,15].

This work has investigated combining irreversible thermogalvanic corrosion with a reversible thermogalvanic redox couple; namely, the

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aqueous  $I^-/[I_3]^-$  redox couple in contact with stainless steel electrodes. The combination of these two thermogalvanic processes are seen to result in significantly enhanced performance relative to solely  $I^-/[I_3]^-$  thermogalvanic redox processes.

## 2. Experimental

Milli-Q™ water (resistivity of  $18.2 \text{ M}\Omega\text{cm}^{-1}$ ) was used throughout. Both bare 304 stainless steel CR2032 battery button cells and platinum-coated CR2032 cells (plasma sputtered, both MTI Corporation, CA, USA) were crimped using a hydraulic press, and thus measurements were made in hermetically sealed casings. All reagents were purchased from Sigma–Aldrich (Castle Hill, NSW, Australia) and used as received.

Electrochemical measurements were performed using a Keysight B2900A Source Measurement Unit, using either Quick IV measurement software or a custom Excel Macro program. Temperature was controlled using the below assembly:

HE|Peltier|ACP|CR2032 cell|ACP|Peltier|HE

where HE is a copper heat exchanger, Peltier is a peltier heater/cooler, and ACP is an aluminum cold plate (all purchased from Custom Thermo-electric, MD, USA), the latter containing an embedded thermocouple. The temperature was thus controlled and maintained to within  $0.1 \text{ }^\circ\text{C}$ , using an Arduino microprocessor.

All current–voltage data points were recorded by steady-state measurements over a 10 min period; the last 5 min was averaged to generate the relevant data points.

## 3. Results and discussion

Aqueous solutions of ferri/ferrocyanide were first investigated in CR2032 battery casings, before investigating iodide/triiodide systems under the same conditions.

The Seebeck coefficient ( $S_e$ ) of  $0.4 \text{ M}$  ferri/ferrocyanide (as  $0.2 \text{ M}$   $K_3[FeCN_6]$  and  $0.2 \text{ M}$   $K_4[FeCN_6]$ ) in deionised water was measured across two flame-annealed platinum wires immersed in this solution housed in a traditional ‘U-tube’ assembly [7] and found to be  $-1.4 \text{ mVK}^{-1}$ . When the same solution was housed in a Pt-sputter coated CR2032 battery casing and measured using a Peltier-based testing apparatus (details in experimental),  $S_e$  was found to be  $-1.3 \text{ mVK}^{-1}$ .

Measurement of the same system in an uncoated (bare, 304 stainless steel) CR2032 battery casing measured  $S_e$  as  $-1.2 \text{ mVK}^{-1}$ . Literature values of  $S_e$  for  $0.4 \text{ M}$  ferri/ferrocyanide span from  $-1.2$  to  $-1.6 \text{ mVK}^{-1}$  [1,2,8,16]. This value is known to be sensitive to the nature and history of the Pt surface; [2,17] the one other report of  $0.4 \text{ M}$  ferri/ferrocyanide being measured in a stainless steel CR2032 battery casing (interior coated with carbon nanotubes) quoted  $S_e$  values of ca.  $-1.1$  and  $-1.2 \text{ mVK}^{-1}$  [8]. The minor differences are attributed to slightly different surface chemistry (cf. ferri/ferrocyanide is a non-ideal outer sphere redox process [18]) and a minor uncompensated temperature drop [8] across the heating block/battery casing/aqueous electrolyte (as encountered by thermogalvanic cells during real applications).

Fig. 1(a) displays the power plots for  $0.4 \text{ M}$  ferri/ferrocyanide in an untreated CR2032 battery casing. As expected, the current–voltage trend was linear between the short-circuit current density ( $j_{ss}$ ) and the open circuit potential ( $V_{OCP}$ ), resulting in a parabolic power output where the maximum power density,  $P_{max} = 0.25*j_{ss}*V_{OCP}$ . As the temperature increased, the  $V_{OCP}$  increased (proportional to  $S_e$ ) and  $j_{ss}$  increased (as a result of improved flux [19]).

Measurement of the Seebeck and current–voltage plots of iodine solutions were significantly more challenging. A solution containing  $0.015 \text{ M}$   $I_2$  in  $0.4 \text{ M}$  NaI was investigated in a Pt-sputter coated CR2032 battery casing, resulting in  $S_e = +0.26 \text{ mVK}^{-1}$ . A value of  $+0.5 \text{ mVK}^{-1}$  has been previously reported for the significantly more concentrated solution  $0.4 \text{ M}$   $I^-/[I_3]^-$  redox couple at pure platinum electrodes [13]. Higher concentration of  $I_2$  resulted in the Pt-sputter coated CR2032 battery casings gradually displaying behaviour identical to an uncoated battery casing (*vide infra*); x-ray photoelectron spectroscopy of the casings before and after use demonstrated the total stripping of the platinum from the surface. The stability of the stainless steel was evaluated by immersing the battery casings into a much larger volume of  $0.4 \text{ M}$   $I_2$  in  $0.8 \text{ M}$  NaI (hereafter referred to as  $0.8 \text{ M}$   $I^-/[I_3]^-$ ) for 5 days. This resulted in essentially zero mass loss ( $0.00 \text{ wt}\%$ ) at  $25 \text{ }^\circ\text{C}$ ,  $0.52 \text{ wt}\%$  at  $45 \text{ }^\circ\text{C}$ , and  $5.6 \text{ wt}\%$  at  $65 \text{ }^\circ\text{C}$ , indicating some corrosion can occur at elevated temperatures.

Using a dilute solution ( $0.005 \text{ M}$   $I_2$  in  $0.4 \text{ M}$  NaI), it was possible to obtain stable and reproducible  $S_e$  values of  $+2.2 \text{ mVK}^{-1}$  ( $\Delta T = 0\text{--}25 \text{ }^\circ\text{C}$ ) in the bare battery casings, an order of magnitude higher than that obtained in the platinum-coated cells. Platinum is known to be an excellent electrocatalyst for the  $I^-/[I_3]^-$  redox system [20], whereas the steel electrodes clearly underwent some form of corrosion, noted

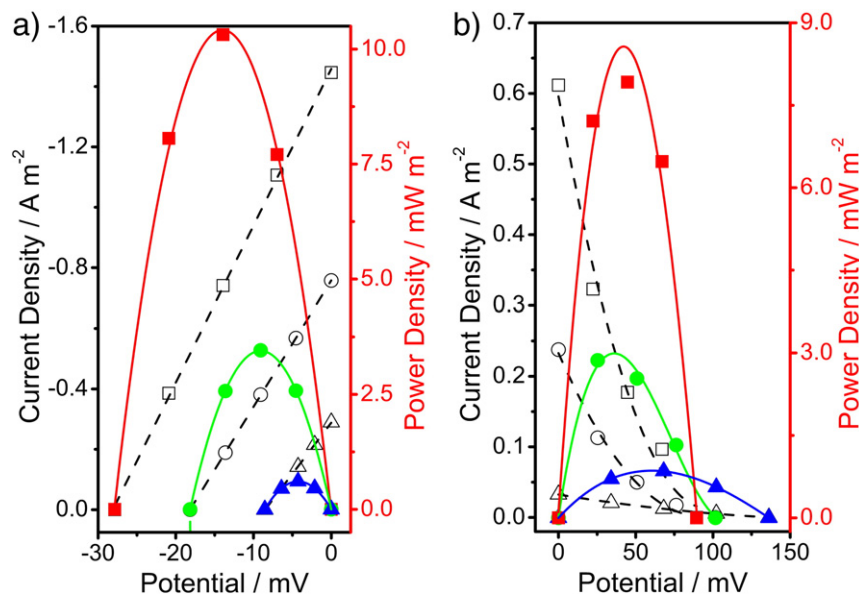


Fig. 1. Power density plots recorded in stainless steel casings with  $T_{cold} = 15 \text{ }^\circ\text{C}$  for (a)  $0.4 \text{ M}$   $[FeCN_6]^{3-}/[FeCN_6]^{4-}$ , at  $\Delta T$  values of  $10 \text{ }^\circ\text{C}$  ( $\blacktriangle$ ),  $20 \text{ }^\circ\text{C}$  ( $\bullet$ ), and  $30 \text{ }^\circ\text{C}$  ( $\blacksquare$ ), and (b)  $0.8 \text{ M}$   $I^-/[I_3]^-$ , at  $\Delta T$  values of  $10 \text{ }^\circ\text{C}$  ( $\blacktriangle$ ),  $30 \text{ }^\circ\text{C}$  ( $\bullet$ ), and  $50 \text{ }^\circ\text{C}$  ( $\blacksquare$ ). Filled symbols correspond to power density values; hollow symbols to current density values.

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