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Thermoelectrochemistry using conventional and novel gelled electrolytes in heat-to-current thermocells☆

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ABSTRACT

Thermoelectrochemistry involves the study or application of temperature-dependant parameters in an electrochemical system. Thermoelectrochemistry can be exploited in non-isothermal cells to form thermogalvanic cells (or thermocells) to convert a temperature gradient into a useful electrical current. However, heat can also transfer and reduce the temperature gradient, while spillage is a potential issue for liquid electrolytes. For this reason, we have investigated aqueous thermocells containing potassium ferricyanide and potassium ferrocyanide ($0.1\,M\,K_3[Fe(CN)_6]/0.1\,M\,K_4[Fe(CN)_6]$) as a gelled electrolyte. Fumed silica and gelatine were not found to be sufficient gelling agents, whereas agar agar (agarose) and beads of poly(sodium acrylate) were found to form effective gelled electrolytes; the latter gel was also self-healing. Thermocells were prepared using commercial CR2032 battery casings, and surface treatments and preparations of the stainless steel electrodes evaluated for their electrocatalytic effects and influence on long-term current output. Emphasis was placed upon body heat harvesting, and preliminary heat transfer modelling through the CR2032 systems also performed. Ultimately, the gelled electrolytes were found to result in more stable power output and effectively frustrate heat transfer through the cells, relative to the un-gelled (liquid) electrolytes. These results will inform the development of both more efficient electrolytes and housings for thermocells.

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1. Introduction

Electrochemistry has revolutionised modern lifestyles and quality of life, particularly in the areas of energy storage and conversion. Thermoelectrochemistry offers a relatively elegant method for the (electrochemical) conversion of a temperature difference into an electrical current [1,2]. It relies upon an entropy difference between the two sides of a redox process; therefore a potential difference (ΔE) can be generated across two electrodes that are directly proportional to the temperature difference between two electrodes (ΔT) and the overall or total entropy change resulting from the redox process. The resulting temperature-dependant potential difference is typically summarised as the Seebeck coefficient, S_e, as shown by equation (1). The entropy changes relate to at least the entropy change due to the electrode reaction, the various entropies of transfer, and the transported entropy of the electrons, as discussed extensively elsewhere [2–5].

The observed potential is also subject to other non-equilibrium effects, such as the Soret effect [2,5,6].

$$S_e = \frac{\Delta E}{\Delta T} \qquad (1)$$

In its simplest incarnation, thermoelectrochemistry is based upon a temperature difference between two electrodes sharing a common redox-active electrolyte [3]. Thus an electrical current stems from a temperature-driven redox process, and thermoelectrochemistry is therefore somewhat analogous to thermoelectric devices where a temperature difference across a semiconductor drives electron or hole transport through said semiconductor [7]. The efficiency of both devices is limited by the maximum possible Carnot efficiency [2].

Thermoelectrics are typically based upon solid-state, rare-earth semiconductors which are incompatible with exposure to repeated temperature gradients and have Seebeck coefficients on the order of $\mu V\,K^{-1}$ [8]. They are therefore reserved for niche applications, typically under extreme conditions, such as space exploration [8]. Conversely, thermoelectrochemical systems can be based on exclusively solid [9], liquid [1] or molten [2] electrolytes, or any combination of solid, liquid and even gaseous [10] electrodes and electrolytes. Significantly higher Seebeck coefficients, on the order

of mV K^{-1}, are taken as standard [1,2]. As the efficiency of heat-to-current conversion is directly proportional to both the temperature difference and the Seebeck coefficient squared, the exceptional Seebeck coefficients of thermoelectrochemical systems have encouraged their investigation for efficient thermal energy harvesting of low-grade sources, such as body heat [11–13]. Nanostructuring the electrodes has also been demonstrated to be relatively facile but highly beneficial [14,15].

The high Seebeck coefficients common to effective thermo-electrochemical systems are typically driven by significant changes in the aqueous solvation sphere around ions [14]. Aqueous solutions of ferricyanide and ferrocyanide are commonly employed as a *pseudo*-standard, by virtue of the redox system's respectable Seebeck coefficient (*ca.* −1.4 mV K^{-1})[7] and relatively fast electron transfer constants (under ideal conditions) [16]. However, a vast range of possible interactions (which have barely begun to be investigated) are also possible entropic driving forces, *e.g.* explicitly coordinating non-aqueous media [14], high spin low spin transitions [17], electrode side reactions [11], electrode intercalation processes [18], solution-phase synergistic interactions [19], *etc.*

Liquid electrolytes are effective for thermoelectrochemical systems (or 'thermocells'), insomuch as they can possess high Seebeck coefficients for certain redox couples, typically possess high solubility for these redox couples, result in a high ionic conductivity of these redox couples, and are flexible [14]. However, they can also leak and suffer from parasitic heat transport, frustrating the formation of sharp and stable temperature gradients [20–22]. Gelled electrolytes represent an attractive and tuneable middle ground, retaining flexibility and potentially high ionic conductivity while frustrating bulk heat conduction and preventing leakage issues.

To date only one report appears to mention gelled electrolytes in the context of thermocells; Manda et al. reported a 'thermocell' using an agar agar gelled electrolyte [23]. However, no comparison was made with non-gelled systems, and only ferricyanide was employed, so balanced redox processes could not have occurred without ferrocyanide present. This likely accounts for why 'Seebeck coefficients' well outside of expected and reasonable values were reported, and which fluctuated randomly *e.g.* 1 M potassium ferricyanide giving Seebeck values of +12.9 mV K^{-1}, −5.2 mV K^{-1} and +4.2 mV K^{-1} at ΔT values of 30, 50 and 70 K, respectively [23]. Brown et al. have investigated the Seebeck coefficient and the reversibility of the inherent thermoelectro-chemistry present in artificial collagen hydrogels and shark-derived hydrogels, to probe the sensory transduction mechanisms of sharks [24].

Conversely, gelling electrolytes in secondary acid batteries have been comprehensively demonstrated to extend lifetime, improve discharge cycle reproducibility, lower electrolyte stratification, reduce leakage of the electrolyte, reduce corrosion, increase resistance to thermal runaway events, *etc* [25,26]. Devices based on gelled electrolytes can also be freely installed and utilised under any orientation, unlike (even extremely viscous) liquid electrolytes [27].

A gel may be defined as a form of matter intermediate between solid and liquid that shows mechanical rigidity, and forms a viscoelastic system where the 'storage modulus' (G′) is larger than the 'loss modulus' (G″) [28]. The simplest and most common test for this is the 'inversion test'; when a sample in a container is turned upside down, a gel will not flow under its own weight (as it possesses a higher G′ than G″), while even a viscous liquid will show significant flow [29].

The formation, structure and characteristics of gels differ depending on the gelling agent used, but generally follows the basis of 'junction zones' [30]. Here distinct phases of gelling agent are present with a solvent in the interstices, to form a three-dimensional heterogeneous network. Such associations in aqueous systems are frequently driven by hydrogen bonding, hydrophobic associations and electrostatic interactions [28].

A significant gelling agent for aqueous solutions is agar agar. It is mainly composed of the polysaccharide agarose, a linear polysac-charide consisting of 1, 3-linked β-D-galactopyranose and 1, 4-linked 3, 4-anhydro-α-L-galactopyranose [31]. When dissolved and precipitated from water (*i.e.* by heating and cooling), a three-dimensional network of cross-linked polymers self-assembles via hydrogen bonding and hydrophobic interactions, which hold the electrolyte solution in place [28]. Silica nanoparticles (in the form of fumed silica) are also widely employed to gel acidic aqueous electrolytes [25,26].

Other polymers are also known to 'immobilise' water, such as zwitterionic or polyionic polymers. For example, poly(acrylic acid) can be cross-linked to form 3D beads (typically via inverse polymerisation methods), converted to the sodium salt, and dried. This results in a free-flowing super-adsorbent powder composed of poly(sodium acrylate) which, when exposed to water, can easily expand within seconds to at least one order of magnitude higher volume and two orders of magnitude higher mass [32].

In this investigation, we have rigorously compared the thermo-electrochemical properties of aqueous ferri/ferrocyanide solutions, both gelled and un-gelled. Conventional agar agar-based gels and novel poly(sodium acrylate)-based gels were selected for in-depth exploration. The interaction of the ferri/ferrocyanide electrolyte with the stainless steel CR2032 battery casings (used to house the samples) necessitated surface chemistry and long-term discharge studies. Heat transport through the cells was also monitored, and modelling employed to explain the observed results. Ultimately, the gelled electrolytes were able to demonstrate improved long-term stability, and beneficially frustrated heat transport, and thus show their significant potential in the context of thermocells.

2. Experimental

2.1. Instrumentation

All cyclic voltammograms were recorded using a μAutolab PGSTAT 101 via Nova software (EcoChemie, Utrecht, The Netherlands), and a Micrux thin film platinum electrode (diameter 1 mm, ED-SE1-Pt, Micrux, Oviedo, Spain). The Micrux electrodes were 'pre-conditioned' in between each experiment by repeatedly scanning between +0.5 V and −0.5 V in aqueous 0.1 M K$_3$[Fe(CN)$_6$]/ 0.1 M K$_4$[Fe(CN)$_6$]; no other form of cleaning or activation was performed. All other measurements were performed inside CR2032 battery casings (MTI Corporation, Richmond, CA, USA). These can contain *ca.* 0.7 mL electrolyte, and were hermetically sealed using an MSK-110 hydraulic crimping machine (MTI Corporation) before use. Platinum-coated CR2032 casings were supplied by MTI Corporation.

Thermoelectrochemical measurements were made using an in-house constructed temperature-control apparatus which has been described in detail elsewhere [14,19]; a schematic of the overall layout is displayed in Fig. S1 in the Supplementary Data. All cells were measured in a thermally "parallel" arrangement, as shown in Fig. S1. This arrangement is distinct from hot-over-cold or cold-over-hot electrode arrangements, which can have significant-ly suppressed or enhanced convection, respectively [33]. Thermo-electrochemical measurements were recorded using a Keysight B2900A Source Measure Unit (TRIO Test & Measurement Pty Ltd, Australia). The open circuit potential and current values determined by measuring continuously for 10 min, and averaging the final 5 min data, unless otherwise specified. Current was