

# Recent trends in thermoelectrochemical cells and thermally regenerative batteries

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## Abstract

Given the ever-growing awareness on global warming, much interest has focused on new and effective ways to manage energy, especially by harvesting and exploiting low temperature heat sources, ubiquitous in the modern environment. Here the holy grail is the direct conversion of heat into electricity especially using thermoelectric devices and in this contribution, we focus on thermoelectrochemical systems.

We give a brief overview of the most common thermally regenerative electrochemical cells developed nowadays with a short overview of their thermodynamic derivation and we collect some of the most recent results in terms of their thermo-electrochemical properties in particular their temperature coefficients. We see that although the most used redox couples are based on  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and their derivatives, thermodiffusion effects and other entropy related phenomena are attracting the attention of the scientific community and boosting astonishing results. On the other hand, thermally regenerative batteries are emerging, showing modest performance.

**Keywords:** thermally regenerative electrochemical cell, TREC, thermo-electrochemistry, temperature coefficient, thermodiffusion, entropy, low-grade heat;

# Introduction

The connection between fossil fuels and global warming produced an ever-growing push toward clear and sustainable energy sources. Although several renewable energies technologies are nowadays available, direct conversion of heat into electricity spun the interest of the scientific community because it can be coupled to existing industrial processes, where for example excess heat needs to be dissipated, and to geothermal [1] and solar energy [2]–[4], where heat is the primary source of energy.

As reported by Forman et al., 72 % of the energy consumed is lost after conversion and 63 % of the available heat stream is at a temperature below 100 °C [5]. Only considering the USA this amounts to almost 19 billion GJ [6].

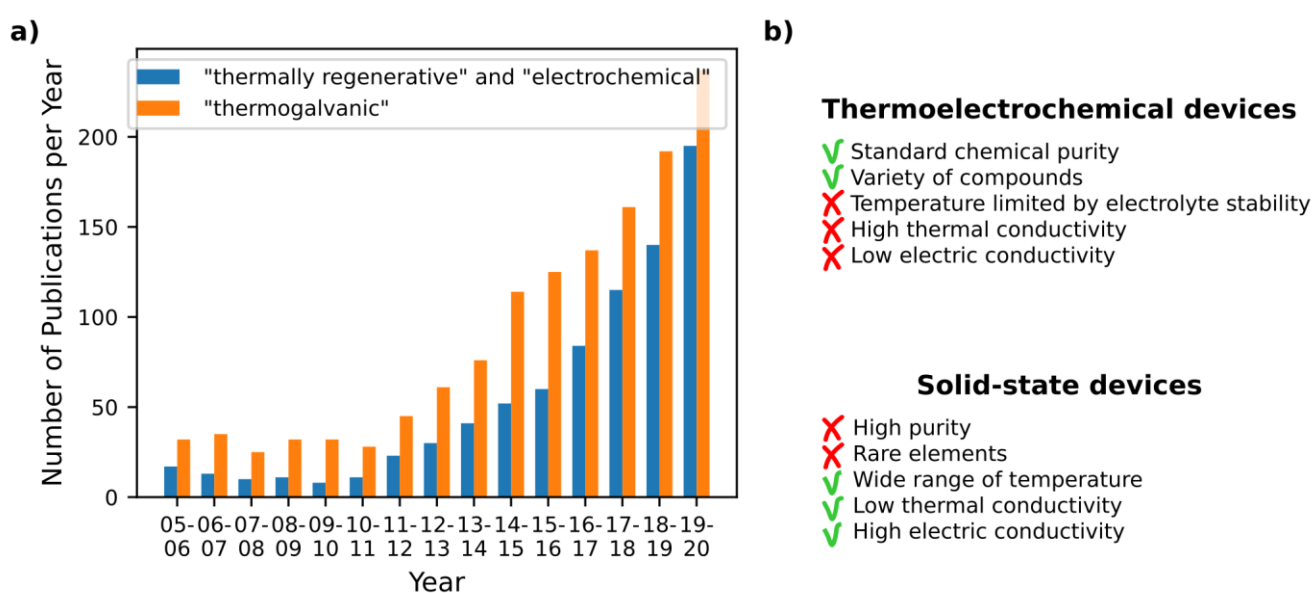
At the moment most of the attention to convert heat into electricity is focused on thermoelectric devices based on semiconductor components, see for example recent review on the topic [7]–[10]. These devices are generally referred to as “thermoelectric generators” TEGs for short. A TEG is composed by an array of N and P semiconductors electrically connected in series. Each N and P semiconductor couple comprises a single thermoelectric module. The modules are placed in parallel between a hot temperature heat source and a cool temperature heat sink. Because of the Seebeck effect, the temperature gradient induces an electromotive forces at the ends of the thermoelectric module which once connected to an electric circuit can be used to harvest electrical energy [7]–[10]. Inverting the current direction the thermoelectric device can move heat between two sources at different temperatures therefore working as cooler or heater [11], [12].

A thermoelectric module can be composed also of an electrochemical cell, in which case it is referred to as thermogalvanic cell. Here instead of the Seebeck effect of the semiconductor junctions the thermal dependence of the electrochemical system is used. However, this is only one of the many strategies in which heat can be converted into electrical energy by the mean of electrochemistry. Already in 1981 Chum and Osteryoung collected a number of works on the topic and coined the term Thermally Regenerative Electrochemical System (TRES) [13]. They defined a TREC as a closed system capable of converting heat into electricity through electrochemical reaction limited by the Carnot efficiency [13].

The thermogalvanic cell was only one of the 7 different types in which they categorized thermo-electrochemical systems. However, the work of Chum and Osteryoung focused on high temperature heat (*ca.* 500 °C) which was at that time suitable for nuclear and aerospace applications.

Nowadays, instead, the focus is on low grade heat with a temperature below 130 °C – or 150-200 °C as there is no clear definition for low-grade heat. This temperature is a perfect match for electrochemical systems operating with aqueous or organic solvent-based electrolyte.

The growing interest of the last decade can be seen from **Figure 1 a)** which shows two bibliographic searches performed through Google Scholar for the terms “thermally regenerative” and “electrochemical” and “thermogalvanic”. Although for both searches the keywords appeared in less than 50 publications per year before 2010, since then both showed a steep growth reaching *ca.* 200 publications per year in 2019-2020. This is still a tenth of the counts for a similar search with “thermoelectric device” for the same year, but it does show the increasing interest in the field.



**Figure 1:** a) Number of yearly publications from 2005 to 2020 referring to “thermally regenerative” and “electrochemical” and “thermogalvanic”. b) Comparison between thermoelectrochemical and solid-state devices for thermoelectric applications.

Compared to a solid-state junction, redox species have the advantage of high temperature coefficients which can be beyond one millivolt per degree, see for example the 1700 long collection made by Bratsch [14]. On the other hand, the Seebeck coefficient for semiconductors is below 250  $\mu\text{V K}^{-1}$  [15].

However, the temperature coefficient is not the sole contributor to thermoelectric performances as also electric and thermal conductivity play an important role, as noted by Quickenden *et al.* who

pointed out that the figure of merit for thermoelectrochemical devices was anyway between two to three orders of magnitude lower than that for thermoelectric devices and the same for Carnot efficiency [16].

Nevertheless, there are recent examples of large figure of merit [17], [18]. Incidentally, deep questioning affected also TEGs in the past [19].

Other differences between devices based on electrochemical and semiconductor systems are summarized in **Figure 1 b)**. In fact, it is noteworthy that applicability of a technology does not only depend on the raw performances, but also on economic viability and sustainability. In this case electrochemical systems are better positioned since they do not require high purification processes and they are based on common and available elements as Fe and Cu (as found by our survey see **Table 2**) against Bi and Te for thermoelectric devices [9]. However, in general, devices based on electrochemical and solid-state junctions have complementary properties.

Although Chum and Osteryoung [13] divided the TRECs into 7 different types according to the how thermal and electric flow of energy was organized, most of the research of the last years focused around the three designs depicted in **Figure 2**.

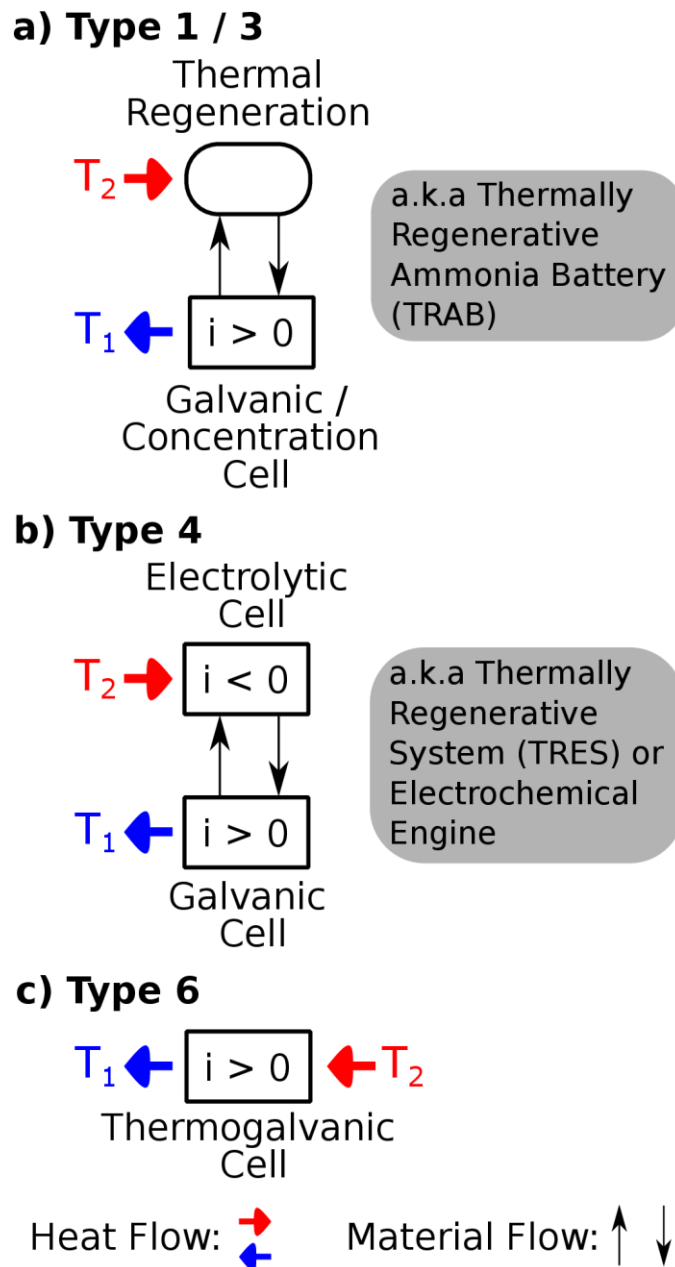


Figure 2: schematic of different types of TREC as described by Chum and Osteryoung [13]. a) Type 1 and 3 comprise a galvanic or concentration cell with thermal regeneration. b) Type 4 comprises a **galvanic** cell with thermal and electrolytic regeneration. c) Type 6 comprises a thermogalvanic cell.

These are *Type 1* (Figure 2 a) which comprises a galvanic cell where redox species are consumed. These species are then regenerated through a thermal process at a different temperature than the galvanic cell. In this case only a thermal input is theoretically necessary. The most famous examples of this TREC type are based on ammonia (Thermally Regenerative Ammonia Batteries TRAB), or acetonitrile [20], [21], but examples employing concentration cells [22] and flow cells

exist [23]. Most of the ammonia-based systems suffer from small cell voltages. We recommend the work of Brogioli and La Mantia for a collection of these technologies [24], [25]. The main advantage of these TREC is the large utilization temperature compared to other types and the possibility to use well-known chemical engineering technologies.

TREC *Type 2* (not shown in **Figure 2**) is similar to Type 1, but it adds a second regeneration step. *Type 3*, instead is equivalent to Type 1, but it employs a concentration cell instead of a galvanic one (Figure 2 a).

In the *Type 4* (**Figure 2 b**) TREC the same electrochemical reaction is performed at two different temperatures either in two separated cells or in the same cell which is thermally cycled. At one temperature the system works as a galvanic cell therefore providing electrical energy, while at the second temperature the cell works electrolytically. In this case both an electric and a thermal input are necessary and it is mostly performed using a single secondary battery which is charged and discharged at two different temperatures as pioneered by Lee *et al.* in 2014 [26]. This TREC type goes also under the name of “electrochemical heat engines” as it resemble the cyclic features of an internal combustion engine [27]–[30].

The performances of these systems are based on the temperature coefficient of the electrochemical system that takes place in the cell, but also on its heat and charge capacity [26].

Notice that elaborated schemes to recover more heat and increase the thermal efficiency of this TREC type exist as for examples those from Long *et al.* [31]–[33].

*Type 5* (not shown in **Figure 2**) is similar to Type 4 but involves also pressure changes.

One of the most adopted TREC type according to our survey is the *Type 6* (Figure 2 c), also known as thermogalvanic cell. Contrary to the other TREC types in this configuration the electrochemical cell works in non-isothermal conditions where one electrode is placed at the temperature  $T_1$  and the second one at  $T_2$ .

As for *Type 4* also in this case the performances are dictated by the thermal coefficient of the electrochemical reaction. Only a thermal input is necessary to run this kind of TREC which can work either continuously, exactly as a thermoelectric device, if the electrodic reactions involve only dissolved species or it needs to be periodically inverted, if the electrodic reaction involves dissolution of a metallic electrode, usually copper, or an intercalation/de-intercalation reaction.

This TREC type is the parallel of a thermoelectric generator. Also, as for TEG cells it can be connected in series taking advantage of opposite thermal coefficients, see for example [34]–[36]. The disadvantage of the *Type 6* TREC is the low cell voltage generated by the system. Systems with a very high thermal coefficient of  $10 \text{ mV K}^{-1}$  and temperature difference of 100 K would generate a

voltage of 1 V. Typical thermal coefficients are *ca.* 2 mV K<sup>-1</sup>, so cell voltages of up to 0.5 V could be reached with a temperature difference of 100 K. Moreover, the electrical conductivity of this cell is dictated by the ionic conductivity of the electrolyte solution which is several orders of magnitude lower than the conductivity of a thermoelectric device. An interesting comparison between a thermoelectrochemical and a thermoelectric generator can be found in the work of Hudak and Amatucci [37]

Finally *Type 7* (not shown in **Figure 2**) involves pressure differences across an isothermal cell.

Of all the TREC types only *Type 6* can produce electrical power in a continuous way. For the other TREC types an inversion of the cell operation is necessary. Alternatively, it is possible to couple two TRECs working at two different temperatures through a heat exchanger [38]. For a TREC *Type 1* such a TRAB, this would involve the transfer of ammonia between the galvanic cells. For the *Type 4* made from a flow battery such as the one proposed by Reinard *et al.* [39], instead, the electrolytes can be pumped between two symmetric flow batteries.

Additional information on applications, such as refrigeration, which involves a TREC can be found in the work of Abdollahipour and Sayyaadi [38].

## Thermodynamic derivation of the temperature coefficient

In this section we will give a brief overview of the thermodynamics governing these systems. The temperature coefficients  $\alpha$  for an electrochemical system can be derived from Gibbs's equation:

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

where  $G$ ,  $H$ , and  $S$  are the Gibbs free energy, the enthalpy, and the entropy of a system at temperature  $T$  and constant pressure. Recalling that the equilibrium potential  $E$  is related to the free energy:

$$\Delta G = -nFE, \quad (2)$$

through the Faraday constant  $F$  and the number of electrons  $n$  exchanged in the reaction.

The temperature coefficient  $\alpha$  can be calculated through the variation of the potential  $E$  with temperature:

$$\alpha = \frac{\delta E}{\delta T} = \frac{\Delta S}{nF} \quad (3)$$

Notice that at constant pressure, the temperature dependence of  $\Delta H$  can be neglected as it relates to the heat capacity at constant pressure and this, even in the case of water, would give a contribution in the order of tens of microvolt. The large entropy variations in chemical systems explains the larger temperature coefficients of thermoelectrochemical systems compared to their solid-state system counterpart.

A more detailed treatment which reports also on the Soret entropy and thermodiffusion phenomena can be found in [40]–[42] and it is worth to check as these can give large contribution to the temperature coefficients as found for example in [18], [43]–[46] compared against a “simple” faradaic reaction, as those collected of Bratsch [14].

It is noteworthy that beyond faradaic and thermodiffusion effects, there exist also thermocapacitive effects in which case the temperature coefficient of the system is given by absorption/desorption phenomena in the double layer as for example in [47]–[49].

In the case of two half-cell reactions which compose either a single cell as for TREC *Type 4* or are placed in series as for a TREC *Type 6*, the total temperature coefficient  $\alpha$  is simply the **difference** of the two independent coefficients:

$$\alpha = \alpha_+ - \alpha_- \quad (4)$$

Finally, from the temperature coefficient and the equilibrium potential, or alternatively from the system enthalpy, the thermoneutral potential  $E_{tn}$  can be derived:

$$E_{tn} = -\frac{\Delta H}{nF} = E - \alpha T \quad (5)$$

which represent the potential at which an electrochemical system neither absorb nor reject heat. We report this last passage here because it gives some limitations in terms of operability of TREC *Type 4* and it usually overlooked.

The relationship between cell potential, reaction direction (current) and heat is reported in **Table 1** which gives a guideline for the design of *Type 4* TRECs, but also for other electrochemical systems. In fact, taking for example water electrolysis which has an equilibrium potential of 1.23 V and a thermoneutral potential of 1.48 V, it is theoretically possible to device an electrolyzer that, working below 1.48 V, would absorb heat from the environment and convert it into chemicals. This is also the reason why some fuel cells could theoretically operate at more than 100% efficiency [50].

Of course, these discussions take in consideration only reversible heat and any additional losses as ohmic drop and polarization and concentration overpotentials would always contribute to irreversible heat production.

The thermodynamic efficiency  $\eta$  of a TREC is given by the ratio between the electrical work produced  $W$  and the heat absorbed  $Q$ :

$$\eta = \frac{W}{Q} \quad (6)$$

If the TREC requires thermal cycling, in  $Q$  apart for the reversible heat ( $T_H \Delta S$  where  $T_H$  is the hot temperature) a term to consider the heat necessary to warm up and cool down the system, which depends on its thermal inertia, is necessary [26]. However, several different formulations can be derived from Eq. 6 even for the same TREC type, see for example the works of Long *et al.* [31]–[33] or Reynard *et al.* [39].

In general the efficiency of a TREC is either reported in absolute terms or as a fraction of the theoretical Carnot efficiency for the given temperatures.

**Table 1:** relation between thermoneutral potential, cell current, and heat.

|                               | $E_{cell} > E_{tn}$ | $E_{cell} < E_{tn}$ |
|-------------------------------|---------------------|---------------------|
| Electrolytic cell ( $i > 0$ ) | Reject heat         | Absorb heat         |
| Galvanic cell ( $i < 0$ )     | Absorb heat         | Reject heat         |

## Survey of recent published articles

To check the pulse of the research in the field of thermoelectrochemistry we conducted a survey on the publications available from 2017 to beginning of 2021. **Table 2** shows the results of this survey, which is not meant to be exhaustive, but it still gives some insight on the most recent trends. For other qualitative and quantitative collections of data we suggest the works of [16], [24], [25], [38], [40], [51].

Most of the screened articles worked around the redox couple Fe(III)/Fe(II), its cyanide complexes, or hexacyanoferrate analogues proving that TREC systems are highly sustainable and environmentally friendly. There is also an almost equal distributions around TREC *Type 4* and *Type 6* followed by smaller amount of works on *Type 1/3* TREC mostly focusing on Thermally Regenerative Ammonia Batteries (TRAB).

The most astonishing result from the survey, is that in the last few years the  $2 \text{ mV K}^{-1}$  wall for temperature coefficients was broken and by taking advantage of thermodiffusion phenomena, phase-

transitions, and Soret entropy some articles reported double digits temperature coefficients with the record held by the work of Fang *et al.* with  $34.5 \text{ mV K}^{-1}$  [18].

Also, what should not be surprising is that thermal efficiencies, relative to that of Carnot, above 10 % were also reported. However, it is duly to point out that several ways exist to calculate the efficiency of a TREC, see for example the works of Long *et al.* [31]–[33], and that this value is considerably more difficult to deal with compared to simple physico-chemical coefficients as the temperature coefficient  $\alpha$ .

On the other hand, many studies used temperatures below  $15 \text{ }^\circ\text{C}$ , which although fair for academic investigation do not represent a realist situation. In fact, on one side  $15 \text{ }^\circ\text{C}$  is below most of average ambient temperature and on the other side it represents a temperature at which electrochemical systems react quite slowly. In both cases this hinders the effective performances.

Contrary to thermoelectric devices, where since the Seebeck coefficients are small and all in the order of  $100\text{-}200 \text{ } \mu\text{V}$ , the performances are mostly dictated by the ratio between the electrical and thermal conductivity, here for the TRECs we see that there is much more room in terms of temperature coefficients and available designs. This is a possible solution for the long-standing trade off between electrical and thermal conductivity which affects the thermoelectric generators.

**Table 2:** survey articles reporting reporting on thermally regenerative electrochemical cell published between January 2017 and April 2020.

| System   | Efficiency<br>(% relative to<br>Carnot efficiency) | Temperature<br>coefficient<br>( $\text{mV K}^{-1}$ ) | Temperature<br>( $^\circ\text{C}$ ) | Reference | Type     |
|--|--|--|-------------------------------------|-----------|----------|
| Ionogel  |  | 34.5   |                                     | [18]      | Type 6   |
| $\text{Fe}(\text{CN})_6^{3-}$<br>/ $\text{Fe}(\text{CN})_6^{4-}$ | 0.006  | 17   | $\sim 36$                           | [43]      | Type 4-6 |
| PVDF-HFP and<br>ionic liquid                                     |  | 17   |                                     | [52]      | Type 6   |
| Acetone and iso-<br>propanol                                     |  | 9.9  | 23-70                               | [53]      | Type 6   |
| NFC and PSSNa  |  | 8.4  | 22.5                                | [45]      | Type 6   |

|   |        |      |       |      |          |
|---|--------|------|-------|------|----------|
| PEO-NaOH  |        | 7    | 0-60  | [44] | Type 6   |
| Capacitive  |        | 6.67 |       | [54] | Type 6   |
| Ag <sub>2</sub> O/Ag and Fe(OH) <sub>2</sub> / Fe   | 9.3    | 5.3* | 20-60 | [55] | Type 6   |
| Graphene oxide, polyaniline, and Fe <sup>3+</sup> /Fe <sup>2+</sup>   | 0.214  | 5    | 30-90 | [56] | Type 4   |
| Fe(CN) <sub>6</sub> <sup>3-</sup> /Fe(CN) <sub>6</sub> <sup>4-</sup> and guanidinium urea                   | 0.0079 | 4.2  | 20-30 | [57] | Type 6   |
| Ionic thermoelectric, capacitive  |        | 4    |       | [58] | Type 4-6 |
| Fe(CN) <sub>6</sub> <sup>3-</sup> /Fe(CN) <sub>6</sub> <sup>4-</sup>  | 11.1   | 3.73 |       | [17] | Type 6   |
| Fe(CN) <sub>6</sub> <sup>3-</sup> /Fe(CN) <sub>6</sub> <sup>4-</sup> and Fe <sup>3+</sup> /Fe <sup>2+</sup> |        | 3.02 |       | [35] | Type 6   |
| V <sup>3+</sup> / V <sup>2+</sup> and Fe(CN) <sub>6</sub> <sup>3-</sup> /Fe(CN) <sub>6</sub> <sup>4-</sup>  | 15     | 3    | 10-50 | [27] | Type 4   |
| Fe(CN) <sub>6</sub> <sup>3-</sup> /Fe(CN) <sub>6</sub> <sup>4-</sup> and methanol                           |        | 2.9  | 10-25 | [46] | Type 6   |
| Co <sup>3+</sup> (py-pz) <sub>3</sub> / Co <sup>2+</sup> (py-pz) <sub>3</sub>                               |        | 2.36 | 25-55 | [59] |          |
| NiHCF and Zn <sup>2+</sup> / Zn   | 25.15  | 2.27 |       | [51] | Type 4   |
| Li <sup>+</sup> / Li organic  |        | 2.02 |       | [60] | Type 6   |

|  |       |       |       |      |        |
|--|-------|-------|-------|------|--------|
| NiHCF  |       | 2     |       | [61] | Type 6 |
| $\text{Fe}(\text{CN})_6^{3-}$<br>/ $\text{Fe}(\text{CN})_6^{4-}$ and<br>$\text{Fe}_2(\text{SO}_4)_3$ / $\text{FeSO}_4$                                     |       | 1.93  | 1-100 | [34] | Type 6 |
| $\text{I}_3$ / I and<br>$\text{Fe}(\text{CN})_6^{3-}$<br>/ $\text{Fe}(\text{CN})_6^{4-}$   | 11    | 1.9   |       | [62] | Type 4 |
| $\text{Fe}(\text{CN})_6^{3-}$<br>/ $\text{Fe}(\text{CN})_6^{4-}$ ,<br>$\text{Zn}^{2+}/\text{Zn}$ , and<br>$\text{Ni}_{0.2}\text{Co}_{0.8}(\text{OH})_2$    |       | 1.87  | 25-55 | [63] | Type 4 |
| $\text{I}_3$ / I and<br>$\text{Fe}(\text{CN})_6^{3-}$<br>/ $\text{Fe}(\text{CN})_6^{4-}$   | 0.119 | 1.8   | 30-60 | [64] | Type 4 |
| $\text{Fe}^{3+}/\text{Fe}^{2+}$  |       | 1.46  | 15-35 | [65] | Type 6 |
| $\text{Fe}(\text{CN})_6^{3-}$<br>/ $\text{Fe}(\text{CN})_6^{4-}$   | 1.4   | 1.43  |       | [66] | Type 6 |
| $\text{Fe}(\text{CN})_6^{3-}$<br>/ $\text{Fe}(\text{CN})_6^{4-}$   |       | 1.4   | 30-70 | [67] | Type 6 |
| $\text{Fe}(\text{CN})_6^{3-}$<br>/ $\text{Fe}(\text{CN})_6^{4-}$   |       | 1.4   | 5-60  | [68] | Type 6 |
| $\text{Cu}^{2+}$ / Cu and<br>CuHCF   |       | 1.28* | 0-50  | [69] | Type 4 |
| Capacitive   |       | 1.21  | 11-64 | [70] | Type 6 |
| Capacitive   |       | 1.2*  |       | [48] | Type 4 |
| $\text{VO}^{2+}$ / $\text{VO}_2^+$ , $\text{VO}^{2+}$<br>/ $\text{VO}_2\text{Cl}$ , $\text{V}^{3+}$ \ $\text{V}^{2+}$ ,<br>$\text{VCl}_3$ \ $\text{VCl}_2$ |       | 1.16  | 20-60 | [39] | Type 4 |

|  |       |       |       |      |          |
|--|-------|-------|-------|------|----------|
| Cu <sup>2+</sup> / Cu and CuHCF  |       | 1.12  |       | [71] | Type 4   |
| Fe(CN) <sub>6</sub> <sup>3-</sup> / Fe(CN) <sub>6</sub> <sup>4-</sup> and gelled electrolyte |       | 1.09  | 5-35  | [72] | Type 6   |
| LMO  | 27    | 1.06  | 10-40 | [73] | Type 4   |
| FeSO <sub>4</sub> / Fe and PbSO <sub>4</sub> / Pb  | 37.7  | 1.06  | 10-80 | [74] | Type 4   |
| CoHCF and AgCl / Ag  |       | 0.89  | 15-45 | [75] | Type 4   |
| CoHCF-pp   | 21    | 0.89  | 10-50 | [76] | Type 4   |
| LMO and NiHCF  |       | 0.843 | 10-70 | [77] | Type 4   |
| Cu <sup>2+</sup> /Cu   |       | 0.798 |       | [78] | Type 6   |
| 2H <sup>+</sup> /H <sub>2</sub> and solid electrolyte membrane                               |       | 0.531 |       | [79] |          |
| LCO  | 13.7* | 0.5   | 20-50 | [80] | Type 4-6 |
| Li intercalation organic solvent   |       | 0.057 |       | [81] |          |

*\* extrapolated; MHCF open-framework metal hexacyanoferrate; for other abbreviations see the specific reference.*

The performance of the thermally regenerative batteries depends on cell voltage, concentration, performance of the electrochemical cell, and performance of the thermal regeneration. These systems have been recently reviewed in detail [25]. Cell voltage and electrochemical cell performance determine the electrical energy output during discharge, while performance of the thermal regeneration determine the heat energy input. Electrical energy output is strongly influenced by concentration of the redox active species, as energy storage density and power density both depend on concentration. High concentrations allow both higher charge storage densities and higher output

currents. Theoretical values can be estimated, but actual values depend on electrochemical kinetics, electrode morphology, operation conditions *etc.* Heat energy requirements for thermal regeneration have been mostly estimated based on for example Aspen simulations, but it is questionable how accurate these simulations are, as for example, the effect of the copper complexation with ammonia is typically disregarded. Therefore, heat energy requirements should preferentially be estimated experimentally, for example by calorimetry, although this can be rather difficult experimentally. On the other hand, simulations can give accurate values for example in cases where boiling point elevations due to the salts are considered and known. This indicates that efficiency values reported in the literature for TREC systems are typically not accurate, but should be treated as estimations. Most accurate values are available for systems where both output electricity and input heat have been estimated experimentally, or for the systems where the input heat can be calculated accurately.

From practical point-of-view, systems should have reasonable power densities. For example, fuel cells operate at up to  $1 \text{ W cm}^{-2}$  [82] and vanadium flow batteries reach  $0.1\text{-}0.5 \text{ W cm}^{-2}$  [83]. In comparison, power densities for thermally regenerative systems reach  $0.01 \text{ W cm}^{-2}$  [25]. Low power output translates to extra costs, as large areas of membranes, electrodes *etc.* are required. Energy storage density depends linearly on concentration. For comparison, vanadium flow battery electrolyte (1.6 M vanadium, cell voltage of *ca.* 1.5 V) stores  $30 \text{ Wh L}^{-1}$ , while low cell voltages and low concentrations of the different thermally regenerative batteries tabulated in **Table 3** limit energy storage densities down to 10-30 times smaller values. Therefore, the next step would be to demonstrate systems able to reach higher cell voltages at high active material concentrations.

**Table 3.** Cell voltages of different thermally regenerative batteries

| System              | Concentration of the active material | Cell voltage (OCP) | Reference  | Type          |
|---------------------|--------------------------------------|--------------------|------------|---------------|
| Cu-NH <sub>3</sub>  | 0.1-0.2 M                            | 0.4-0.5 V          | [84], [85] | <i>Type 1</i> |
| Cu- ethylenediamine | 0.1 M                                | 0.6 V              | [86]       | <i>Type 1</i> |
| Ag-NH <sub>3</sub>  | 0.1 M                                | 0.4 V              | [87]       | <i>Type 1</i> |
| I <sub>2</sub>      | 17.5/1.7 mol-%                       | 0.245 V            | [23]       | <i>Type 3</i> |
| Br <sub>2</sub>     | 20/1.7 mol-%                         | 0.45 V             | [88]       | <i>Type 3</i> |

|                                     |        |   |      |   |
|-------------------------------------|--------|---|------|---|
| Cu-acetonitrile-H <sub>2</sub> O    | 0.1 M  | 0.6 V                                       | [20] | <i>Type 1</i>                                     |
| Cu-acetonitrile-propylene carbonate | 0.15 M | 1.3 V                                       | [21] | <i>Type 1</i>                                     |
| Cu-Zn-NH <sub>3</sub>               | 0.1 M  | 1.38 V<br>(discharge)<br>0.72 V<br>(charge) | [89] | <i>Type 1<br/>requiring charge<br/>afterwards</i> |

Recent research on this field has been focused to optimize different components of the electrochemical systems, including cell architecture and membranes [90], and electrodes [91], testing decoupled electrolytes [85], or developing completely new approaches for electrochemical discharge, for example fluidized bed reactors [92]. While this research is very useful for optimizing system performance, novel approaches employing systems with higher cell voltages and concentrations are required to develop practical devices. Two systems in **Table 3** point towards this direction: non-aqueous copper-acetonitrile system with 1.3 V cell voltage, and the bimetallic Cu-Zn-NH<sub>3</sub> system. While solubility of up to 1.5 M of Cu could be reached in acetonitrile [93], this system suffers from high resistance of the non-aqueous solvent, and high cost of the different components. Bimetallic system requires both thermal and electrical charge and both shows poor charge storage density and efficiency. However, concentrations limits of this system have not yet been explored.

## Conclusion and Future Perspective

With this work we gave a short overview of thermally regenerative electrochemical cells (TRECs) and their working principles and thermodynamic derivations. Also, we checked the most recent trends both in terms of published output and in terms of quantitative parameters, such as working temperature, efficiency, temperature coefficients, and chemistry. We found that extremely high temperature coefficients and efficiency were recently reported mainly boosted by tuning of thermodiffusion effects. **Thermodiffusion, thermoionic, and thermocapacitive phenomena represent a fertile field which should be pursuit for future investigation and development.** However, in our opinion greater performances can be achieved **by working above room temperature where ionic conductivity and electrokinetics are higher.** In future, attention should be focused not only in **achieving high efficiencies but also higher power densities.**

For thermally regenerative batteries, most of the reported systems suffer from low cell voltages and concentrations, resulting in too low energy storage densities and power densities for practical applications. Therefore, future work should be focusing in improving cell voltages, for example by utilizing bimetallic systems, and on increasing concentration of the active materials.

In general, long term thermal stability for the electrolytes, electrodes, and cell materials are not considered. However, these should not be overlooked as they become particularly important when working at higher temperatures and with more concentrated solution which are both requisites to achieve high energy and power densities.

**Declaration of interest:** none

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