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Thermodynamic study of a distiller-electrochemical cell system for energy production from low temperature heat sources

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ABSTRACT

The "thermally regenerable batteries" have been proposed for exploiting the heat sources at very low temperature, below 150° (e.g. low-concentration solar and industrial waste heat) for production of electrical energy, in particular for small power applications. In this case, traditional techniques, such as organic Rankine cycle, Stirling engines and solid-state devices based on Seebeck effect, are not economically viable. In particular we consider an electrochemical method working with a closed cycle: a salinity-gradient-power device produces electrical current by consuming the concentration difference between two solutions; the mixed solutions it produces are sent to a distiller which restores the concentration difference, in turn exploiting the low-temperature heat source. Unfortunately, the efficiency of the devices proposed up to now is low. In this manuscript, we present for the first time a theoretical analysis of the whole cycle, in order to enable an educated choice of solutes and solvents with respect to the efficiency in the conversion of heat into electrical power. We find that the main requirement is a high boiling point elevation; minor advantages are obtained by solutions with a high latent heat of vaporisation and low specific heat capacity. The first two requirements could appear counter-intuitive, since they are detrimental in the case of distillation processes *per se*. While the above-mentioned requirements are connected to fundamental limitations of the energy and exergy efficiency of the device, the electrochemical parameters mainly affect the power density. Our results allow to devise solutions for single-effect processes that give a high exergy efficiency for very low temperature heat sources, i.e. to approach the Carnot cycle limit (e.g. 11% of energy efficiency for a temperature difference of 40 K), competitive with the more traditional techniques but much cheaper and easily down-scalable.

1. Introduction

The free energy contained in solutions with different concentrations can be tapped and converted into electrical energy by means of the so-called SGP ("salinity gradient power") techniques, e.g. by means of a concentration-difference electrochemical cell [1].

Various SGP techniques have been proposed for the conversion of the concentration differences into current. They were often conceived as a mean for the production of completely clean and renewable energy by exploiting the naturally occurring solutions with different concentrations [2–4]. Such solutions include river and sea waters, and brines from salt lakes (e.g. Dead Sea) [5], from coal-mines (produced by dissolving geological deposits) [6], and from salterns [7].

Recently, various researchers proposed to apply instead these techniques in situation in which the difference in concentration is produced by means of distillation [8–11] (see Fig. 1). In other terms, these authors proposed to use the following thermodynamical cycle: the solutions with different concentrations enter into the SGP cell, which exploits part of the available mixing free energy. The outgoing solutions are then completely mixed and are sent to a distiller, where the concentration difference is restored so that a new cycle can take place. The whole device, which operates in closed-cycle with respect to the involved masses, can be considered as a HTCC (heat-to-current converter), conceived for exploiting low-temperature heat sources.

In the literature, a thermodynamical analysis of such a cycle is apparently lacking. The present work aims at finding how the efficiency of the HTCC depends on the thermo-physical parameters of the solutions, allowing for a selection of the solutions that gives a

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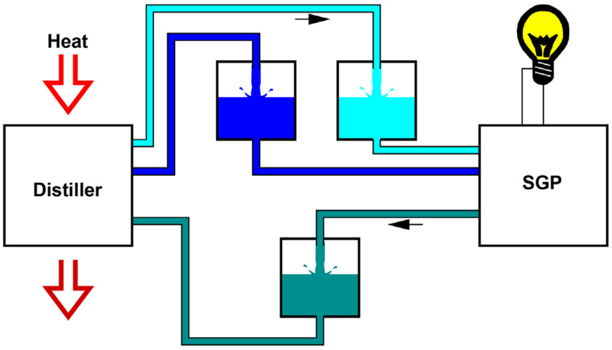

Fig. 1. Scheme of the device that produces electrical energy by exploiting a low-temperature heat source.

high energy efficiency η (the ratio between the produced electrical work and the heat adsorbed from the heat source) and exergy efficiency η^B (the ratio between the produced electrical work and the maximum useful work that can be ideally extracted; in the present case, since the HTCC is analogous to a heat engine, the latter is the work extracted by a Carnot cycle).

It will be shown in Sect. 3 that the efficiency improves as the boiling point of the more concentrated solution increases. A weaker improvement is obtained by using a solvent with a high latent heat of vaporisation and with a low specific heat capacity. Such parameters will constitute clues for the selection of candidate solutions to be used in our HTCC. In principle, the efficiency of the HTCC can reach an energy efficiency η close to that of a Carnot cycle working between the boiling point of the more concentrated solution and the boiling point of the pure solvent. This means that the exergy efficiency η^B is high (ideally close to 100%) only when the boiling point elevation matches the available temperature difference. If we aim at exploiting temperature differences of the order of 40 K or more, a so high boiling point elevation can be obtained only with very concentrated solutions, at molar fractions of 20–30%; only a few solute are thus suitable.

It is worth noting that the role of the first two parameters (i.e. boiling point elevation and latent heat of vaporisation) could be counter-intuitive, since they have a detrimental effect in distillation. The question can be settled by remarking that our aim of increasing the free energy content of the solution is different from that of distillation, that aims at the maximum production of concentrated solution or distillate.

The overall energy efficiency η is the product of the energy efficiencies of the distiller stage and of the SGP cell:

$$\eta = \eta_{dist}\eta_{SGP}, \tag{1}$$

where η_{dist} is the energy efficiency of the distiller in converting heat into the mixing free energy of the solutions and η_{SGP} is the energy efficiency of the SGP device in converting the free energy into electrical energy. Also the exergy efficiency η^B can be factorised:

$$\eta^B = \eta^B_{dist}\eta_{SGP}. \tag{2}$$

In principle the SGP stage, working isothermally, can extract all the free energy of the solutions, and thus we define its exergy efficiency as η_{SGP}. Here the exergy efficiency of the distiller η^B_{dist} is defined as the ratio between the free energy of the produced solutions and the maximum useful work that can be ideally extracted (by a Carnot cycle in our case).

In this paper, we will consider an SGP device based on electrochemical principles of operation, so that the HTCC we study falls in the broader category of the "thermally regenerated electrochemical cells" [12], in which the regeneration takes place by means of a thermal effect (either physical, such as distillation, or chemical) and the electrochemical cell exploits a composition difference between solutions. Some examples are given by copper redox flow battery [13] or cells based on complexation of copper ions by ammonia [10]. In various patents (e.g. WO 2012012767 and US 4292378), the electrochemical SGP devices is based on RED (reverse electrodialysis) [14–16], in which the feed solutions are sent through a stack of ion-exchange membranes; the ion diffusion which takes place across the membranes constitutes a current that can be extracted from the cell. Although all the cited techniques allow, at least in principle, to reach a high efficiency η_{SGP} of the electrochemical SGP device (50%–80%), the overall energy efficiency η is much lower, due to the low efficiency of the distiller stage. In the "thermally regenerable batteries" proposed in literature, the boiling point elevation is small, and this leads not only to a low energy efficiency η but also to a low exergy efficiency η^B at temperature differences of more than 10 K. Up to now, this obstacle has not been recognised in literature as the most limiting element of the technique.

A novel family of SGP techniques has been recently introduced for the exploitation of naturally occurring salinity differences: it includes the CapMix ("capacitive mixing") [17–23] and "mixing entropy battery" or BattMix ("battery mixing") [8,24]. The latter technique can be efficiently applied also to the artificially produced solutions used in the HTCC; indeed, BattMix devices specifically designed for lithium chloride and zinc chloride solutions have been studied [17,8,25,26].

The BattMix technology allows to reach higher overall efficiencies. The reason resides in the possibility of exploiting unusual and much more concentrated solutions with respect to the membrane-based RED technique; this allows to reach a higher efficiency η_{dist} of the distiller stage. For example, we will show that a HTCC cycle working with a BattMix cell using aqueous zinc chloride solutions can theoretically reach an energy efficiency η of 8% with the very small temperature difference of 40 K [25] and an exergy efficiency η^B of 70% (see Sect. 2.1).

The thermo-physical properties of the solutions, relevant for the operation of the distiller stage, lead to fundamental physical limitations of the energy efficiency η_{dist} and exergy efficiency η^B_{dist}, as shown in Sect. 3. The same thermo-physical parameters also determine the voltage (or voltage rise) of the SGP cell and the maximum work production (attained at vanishing current). In practical conditions of power production, relevant energy losses take place due to the overvoltage, affecting the efficiency η_{SGP}; however, in Sect. 2 we show that, under the (often valid) assumption that the overvoltage is linear in the current, it is possible to trade-off the power output for the efficiency η_{SGP}, thus reaching a reasonably high energy efficiency (e.g. 80%) although at the expense of the power output density.

We now make a comparison between our approach for the heat-to-current conversion and the more traditional ones. We recall that the conversion of heat to mechanical work is traditionally obtained by means of heat engines (see for example [27]), and in the cases of low temperature sources the Stirling motors or organic Rankine cycle devices are proposed. However, the quest for alternative methods, less relying on moving parts, is an important research field.

The HTCC we propose has several advantages over the traditional solutions. First of all, thanks to the limited presence of moving parts, the devices need a very limited amount of maintenance, making them suited for domestic and small-scale applications. Another remarkable advantage of this scheme is that it can produce electric power on demand, because the solutions produced by the distiller during a few hours (e.g., around noon for solar