

## Preview

# A New Take on Electrochemical Heat Engines

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Developing a heat engine that can efficiently use waste heat from another process has been a grand challenge for over 50 years. However, a new article in *Energy & Environmental Science* by Poletayev et al. introduces a new electrochemical heat engine concept that can overcome previous limitations.

The article by Poletayev et al.<sup>1</sup> presents a fundamentally new approach to the problem of using a heat engine to convert a fraction of wasted heat, from some arbitrary process, to electricity. The concept and analysis presented in the paper is elegant and has been generalized to an entire class of systems/devices that utilize this new operating characteristic. For this reason, it is a very important paper that paves the way for what could essentially become a new field, as others have also begun developing similar concepts.<sup>2</sup>

To explain how their concept works, it is useful to focus on just one of their example systems. Consider the following thought experiment. Imagine you have a high-temperature electrolysis system (i.e., an electrolyzer) that is used to split water and make hydrogen and oxygen ( $2 \text{H}_2\text{O} \rightarrow 2 \text{H}_2 + \text{O}_2$ ) that is nominally designed to operate at  $900^\circ\text{C}$ .<sup>3</sup> For this reaction to occur you must supply a voltage (i.e., electricity) that will drive the oxygen in  $\text{H}_2\text{O}$  to ionize, gaining two electrons, which it will later give up on the other side of an electrolyte membrane.

Now let us consider an important feature of such a device, namely that the amount of electricity that must be supplied to power the electrolyzer is a function of temperature. As the temperature of the device/reaction increases, the equilibrium in the gas shifts

and less electricity is required (i.e.,  $\Delta G$  decreases with increasing temperature) and more heat is required. At roughly  $3,000 \text{ K}$ , the reaction can even proceed spontaneously with only heat and no electricity input, since the  $T\Delta S$  term, which corresponds to the heat input required, becomes equal in size to the  $\Delta H$  term, rendering  $\Delta G = 0$ . To understand their paper it is important to appreciate this effect and why it happens. If, for example, one were to put an amount of steam into a closed vessel and begin heating it, as the temperature increases a fraction of the water molecules will spontaneously split and form  $\text{H}_2$  and  $\text{O}_2$ . The hotter the gas becomes, the greater the fraction of the molecules that will convert to  $\text{H}_2$  and  $\text{O}_2$ , as described by the equilibrium constant. What drives this to happen is the fact that the reaction  $2 \text{H}_2\text{O} \rightarrow 2 \text{H}_2 + \text{O}_2$  involves an increase in entropy. This is intuitive because one changes from having two gas molecules ( $2 \text{H}_2\text{O}$ ) to three ( $2 \text{H}_2 + \text{O}_2$ ), and the three ( $x, y, z$ ) new degrees of freedom introduced by the formation of the additional molecule correspond to an increase in the total number of microstates accessible to the system. As a result, this corresponds to an increase in entropy for the reaction. This effect is what underlies the innovation described in the paper. Since the equilibrium concentrations of each species in the gas phase are temperature dependent, and the reaction can

partially occur on its own due to an increase in temperature, a lower electrical driving force is required to break the bonds and operate the electrolyzer as you increase in temperature.

Now consider a completely separate second device, namely a high-temperature hydrogen fuel cell, that is initially independent and uncoupled from the electrolyzer. This device is essentially the same as the electrolyzer, except that it operates in reverse—specifically it leverages the driving force for  $\text{H}_2$  and  $\text{O}_2$  to want to react, in order to generate a voltage (i.e., electricity output). This device takes in  $\text{H}_2$  and  $\text{O}_2$  and outputs  $\text{H}_2\text{O}$ , and because it is the same reaction occurring in the electrolyzer, the voltage it produces is also temperature dependent—i.e., it is the same voltage versus temperature relation as the electrolyzer and for the same exact reasons. However, if you imagine that the fuel cell is operated at  $500^\circ\text{C}$  and the electrolyzer at  $900^\circ\text{C}$ , it is clear that the voltage required by the electrolyzer is actually lower than the voltage output of the fuel cell. This difference is precisely what is used in their new concept to provide a continuous net electrical output.

To understand how to take advantage of this, now imagine that you electrically connect the two devices so that the fuel cell powers the electrolyzer. Based on the higher voltage produced by the fuel cell, there is actually some additional/residual voltage that can be used to power an external load between the two devices. The next step is then to realize that since the same reaction is occurring in both devices (i.e.,

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the electrolyzer and fuel cell), just in different directions, the reactant and product streams for both devices can also be connected to keep all the chemical species in a closed loop. In this way, the electrolyzer takes in  $\text{H}_2\text{O}$  and outputs  $\text{H}_2$  and  $\text{O}_2$  at the exact same rate that the fuel cell correspondingly consumes the product  $\text{H}_2$  and  $\text{O}_2$  from the electrolyzer and outputs  $\text{H}_2\text{O}$ . However, at this point it may still not be obvious how this connecting of two devices results in a heat engine. To understand this, one must revisit the details of the reaction.

In the electrolyzer, one supplies electricity, but it is important to also note that the reaction is still endothermic ( $T\Delta S > 0$ ). This is because the reaction involves an increase in entropy (i.e., going from two, up to three gas molecules). This entropy must come from somewhere, namely heat. It can be supplied by extra electricity being converted to heat locally (i.e., joule heating) where the reaction takes place, which is entropy generation. Or it can be supplied by an external entropy transfer into the system as heat, which is how their new device makes use of a heat input. Conversely, the opposite happens in the fuel cell. Since the reaction involves a decrease in entropy, from three gas molecules down to two, the entropy must go somewhere, which is why the reaction is exothermic ( $T\Delta S < 0$ ) and it must release heat. The heat released carries away the remaining entropy, which is the difference between the three gas molecules versus two. The key is to then realize that when one connects the fuel cell and electrolyzer in this clever way, the entire

system operates as a heat engine, where the two separate devices are simply connected electrically (i.e., so the fuel cell powers the load in addition to the electrolyzer) and chemically, so that all species are internally recycled, making the system closed looped. With this approach, one can operate the two devices in a continuous manner where the electrolyzer takes in heat to feed its endothermic reaction, keeping it hot, while the fuel cell releases heat and must be cooled so it doesn't overheat. In addition, they point out that in order to make this combined system efficient, one should exchange the heat between the respective reactant and product streams, which is straightforward.

The paper presents this as one of many potential example systems that can operate this way and makes many comparisons to thermoelectrics. The comparison to thermoelectrics is warranted from two perspectives: (1) because thermoelectrics are one of the main competing technologies focused on direct conversion of waste heat to electricity and (2) because the properties of their new concept can be likened and directly compared to thermoelectrics. In this sense, their scheme offers a major advantage over traditional thermoelectrics, which operate based on the Seebeck effect and suffer from the fact that the most important material properties are coupled. Specifically, this new class of devices can allow one to separate the electrical conductivity coupling to the effective Seebeck coefficient, since the electrons can be delivered by external wires that are highly electri-

cally conductive and are independent of the redox couple's thermodynamics, which dictate the effective Seebeck coefficient. The second critical aspect is the fact that the heat leakage that usually occurs across a single leg of a thermoelectric device, via heat conduction in the thermoelectric material, can now be completely decoupled from the other device properties that dictate its figure of merit. Most specifically, the heat leakage that occurs now happens along the interconnecting fluid, as axial conduction in the gas, as it flows through the heat exchangers in between the two devices (i.e., electrolyzer and fuel cell). Each device operates isothermally, but individually at different temperatures. This is a very important advantage because the distance between the two devices can simply be increased to add thermal resistance, without much impact at all on the fluid transport speed, which is dictated by the gas diffusion kinetics and could be accelerated by a pump/compressor if desired. In this way, the paper presents a new class of technologies that warrant further development and have major performance advantages over traditional thermoelectrics.

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