Continuous electrochemical heat engines

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Outline

Thermoelectric effect

The thermoelectric effect is the direct conversion of temperature differences to electric voltage and vice versa via a thermocouple. Seebeck coefficient: $S = dV/dT$.

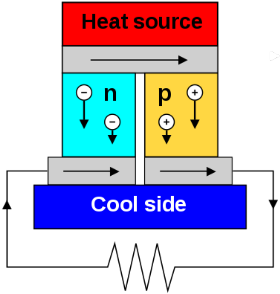


Figure 1: A thermoelectric circuit composed of materials of different Seebeck coefficients (p-doped and n-doped semiconductors), configured as a thermoelectric generator.

Thermal-to-electric heat engine

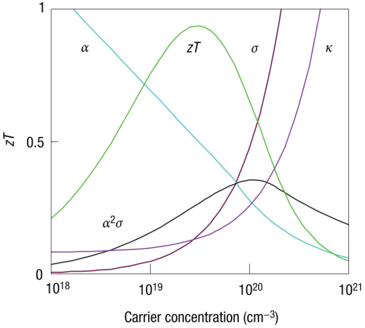


Figure 2: Optimizing ZT through carrier concentration tuning

How to imporve ZT when k and σ are closely coupled?

- Thermoelectric figure of metrit : $\mathrm{ZT} = \mathrm{S}^2\sigma\mathrm{T}/\mathrm{k}$
- $\mathrm{k} = \mathrm{k_e} + \mathrm{k_p}$
- Wiedemann-Franz law: $\mathrm{k_e} = \mathrm{L}\sigma\mathrm{T}$

Abstract

Main challenge

The main challenge in direct heat-to-electricity conversion is to experimentally realize continuous thermodynamic cycles that sidestep the coupling of entropy, heat and charge transport and operate across a broad range of temperatures.

This work

This work leverages the progress in flow batteries and fuel cells to experimentally demonstrate continuous electrochemical heat engines based on two redox-active working fluids separated by ion-selective membranes.

Redox-Flow Battery

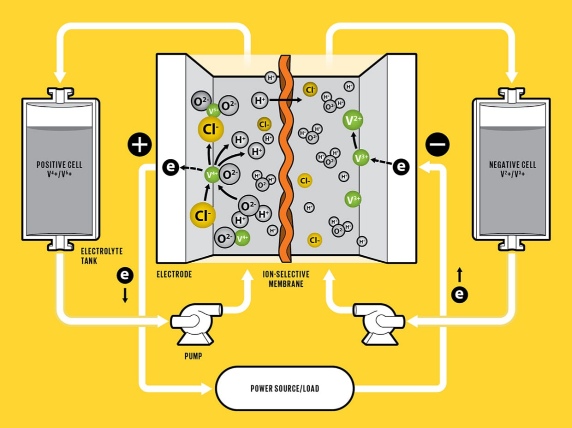


Figure 3: The Vandium Redox-Flow Battery.

Convert chemical energy into electric energy.

Analogy

Temperature coefficient: $\alpha = \mathrm{dV/dT}$

$$(\alpha_1 - \alpha_2)\Delta T \rightarrow (\Delta S_1 - \Delta S_2)\Delta T/nF = \Delta V_{OC}$$

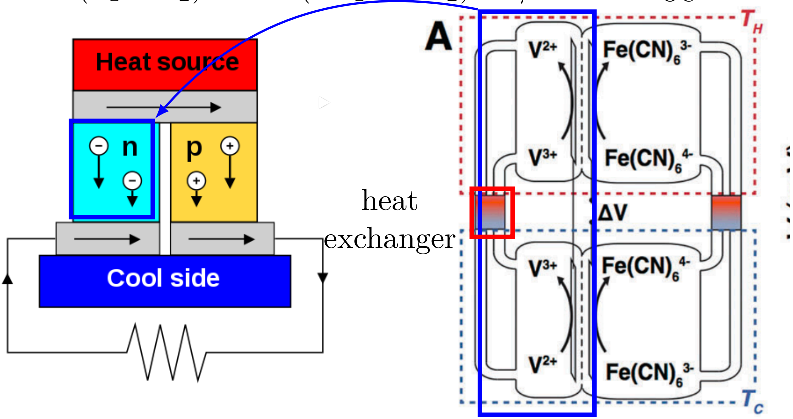
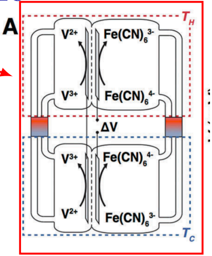


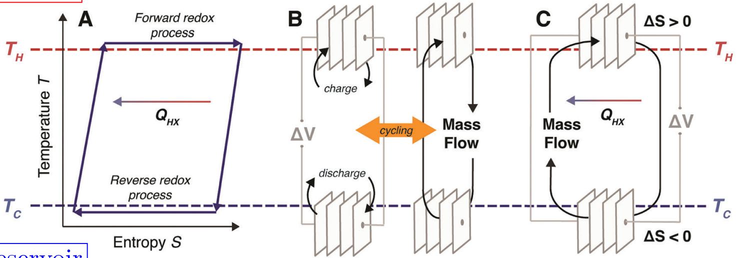
Figure 4: Continuous electrochemical heat engine. Convert heat into electric energy.

Continuous electrochemical heat engine

- Entropy transport:
  reaction at constant temperature.
- Charge transport:
  membranes: ion; electrodes: electron.
- Mass and heat transport:
  electrolyte flow



Hot reservoir



Cold reservoir

Figure 5: Continuous electrochemical heat engine. Convert heat into electric energy.

Electrical and thermal irreversibilities

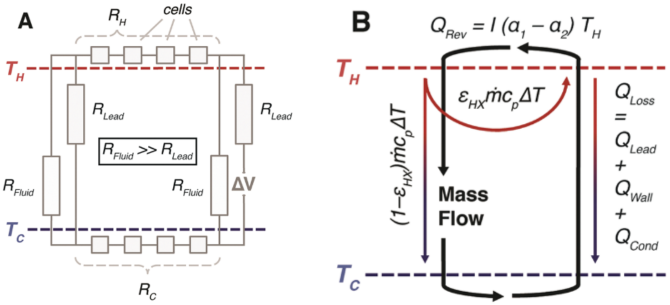


Figure 6: Electrical and thermal irreversibilities in the continuous electrochemical heat engine.

. . . .

$$\eta = \frac{\mathrm{I}\left(\Delta\mathrm{V_{OC}} - \mathrm{I}\left(\mathrm{R_C} + \mathrm{R_H}\right)\right) - \mathrm{I^2R_{Lead}} - \mathrm{P_{aux}}}{\mathrm{IT_H}\left(\alpha_1 - \alpha_2\right) + \mathrm{Q_{Loss}} + \left(1 - \varepsilon_{\mathrm{HX}}\right)\dot{\mathrm{m}}\mathrm{c_p}\Delta\mathrm{T}}$$

Dependence of cell potentials on temperature.

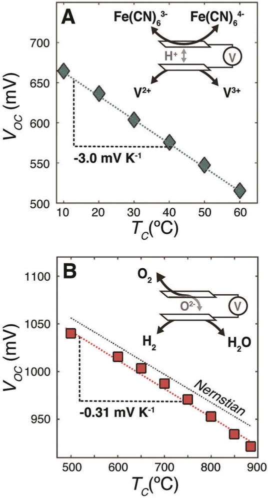
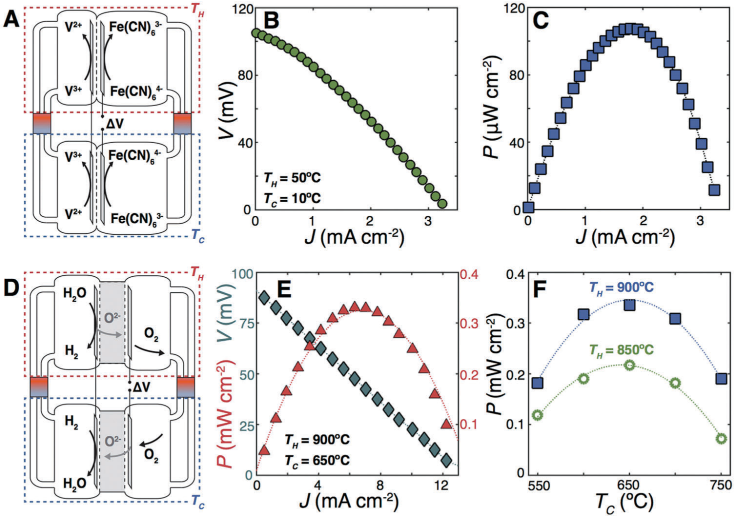


Figure 7: Open-circuit voltages of electrochemical cells.

- the slope of the line is equivalent to the total thermopower $(\alpha_1 - \alpha_2)$.
- $\Delta V_{OC} = (\alpha_1 - \alpha_2)\Delta T$.

Polarization curve and maximum power



$\eta \approx 0.15\eta_c$

Figure 8: Two electrochemical heat engines developed in this work.

Efficiency and power

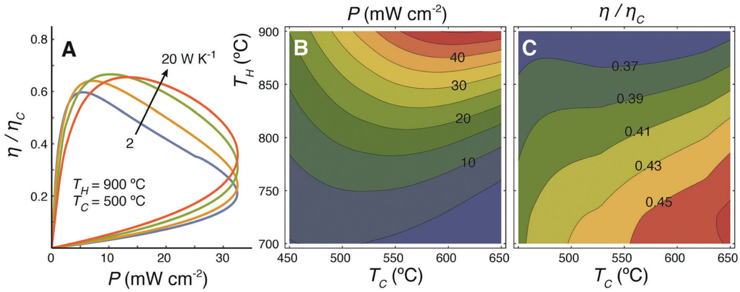


Figure 9: Simulations of gas-based continuous electrochemical heat engines. (A) Effiency and power parametrized by the current-vlogate curves. The four curves correspond to a counterflow heat exchanger rated for 2, 5, 10, and 20 W K^{-1}. (B)-(C) Maximum power density and efficiency as a function of T_H and T_C.

Efficiency and power

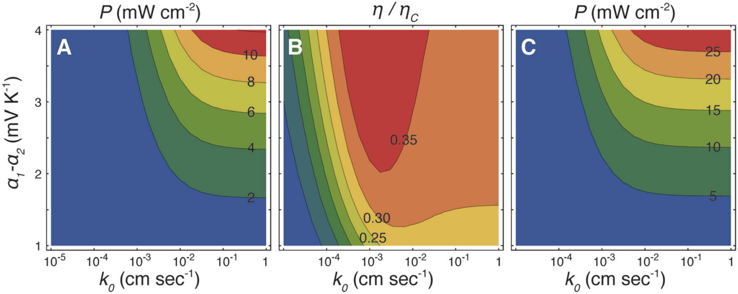


Figure 10: Simulations of liquid-based continuous electrochemical heat engines. Maximum power density (A) and efficiency at the maximum power point (B) for a heat engine operating between 50 °C and 10 °C as a function of redox-active fluid properties α and k0, with concentrations of active species corresponding to the experimental system. (C) Concentrations of activate species increased to 15M.

Comparison

Table 1: Comparison between solid-state thermoelectrics and continuous electrochemical heat engines developed in this work.

	Solid-state thermoelectrics	Electrochemical heat engines
Mechanism	Temperature dependent thermoelectric voltage	Temperature dependent reaction potential
Parameter	Seeback coefficient: $\alpha = \mathrm{dE}/\mathrm{dT}$	Thermopower: $\alpha = \Delta \mathrm{S}/\mathrm{nF}$
Thermal transport	Conduction	Convection of working fluids
Electrical transport	Conduction	Ion-conductance and conduction in the electrodes
Stacking	Will increase heat leaks	Won't increase heat leaks
Efficiency	5% - 15% η_c	Over 30%η_c

Conclusion

- The work demonstrated two electrochemical heat engines operating in very different temperature regimes.
- Based on system modeling, the continuous electrochemical heat engine can scalably reach maximum power point efficiencies well over 30% of η_c under diverse operating conditions.
- By decoupling thermal and electrical entropy generation pathways, the work demonstrated effective energy conversion in regimes heretofore inaccessible to TE, TG, regenerative, or other thermal-fluid heat engines.

Thank You!