Thermoelectric Energy Conversion: Science and Engineering Challenges and Opportun

r Group

Arun Majumdar

Departments of Mechanical Engineering &

Materials Science & Engineering (courtesy), Stanford University

Department of Photon Science, SLAC

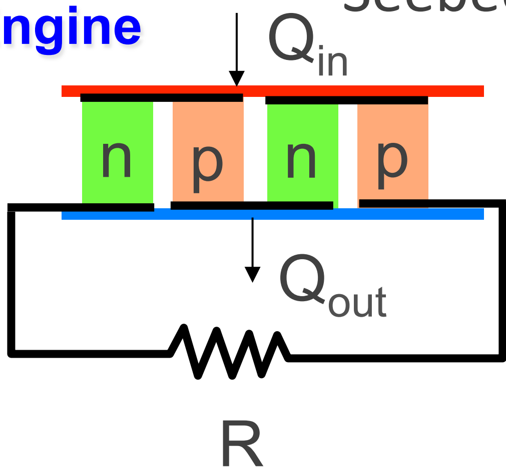
rd | ENGINEERING
Engineering

"Any sufficiently advanced technology is indistinguishable from magic." Arthur C. Clarke

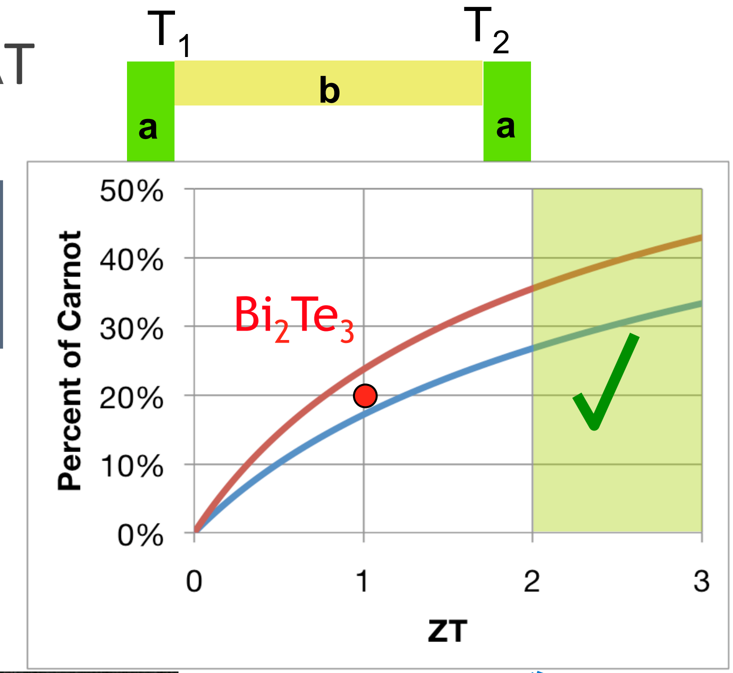
Thermoelectricity & Energy Conversion

Seebeck Coefficient, $S = V/\Delta T$

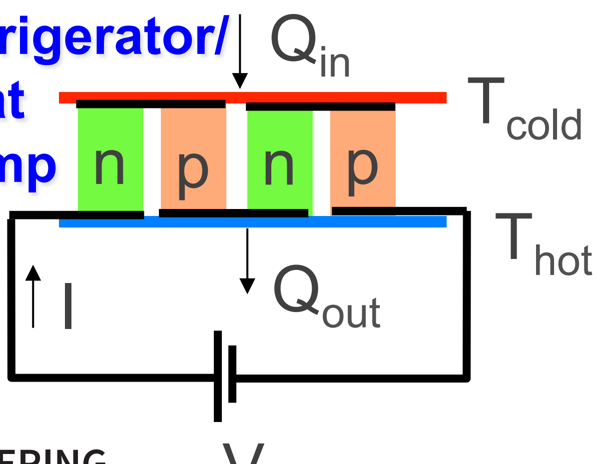
Engine

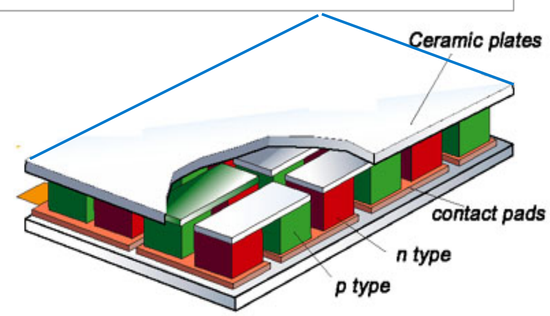


$$ZT = \frac{S^2 \sigma T}{k}$$



Refrigerator/ Heat Pump

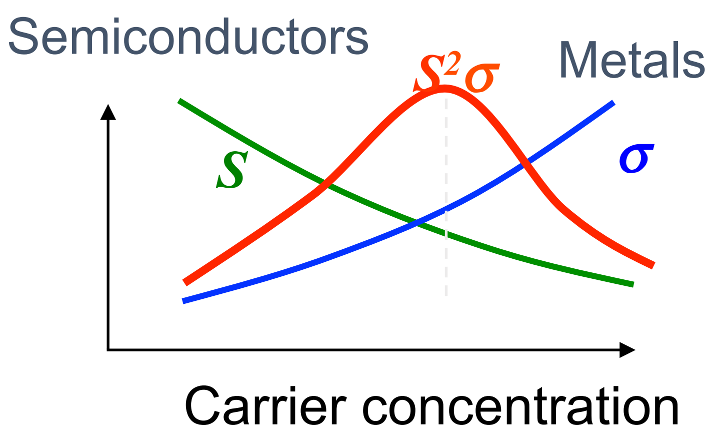


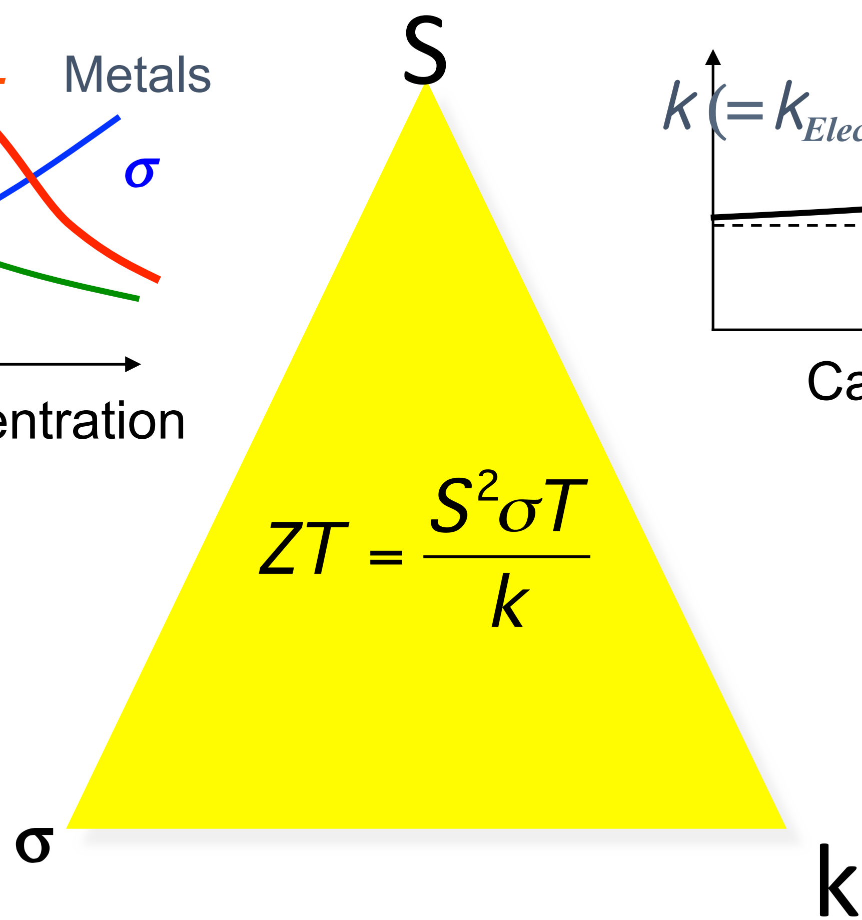


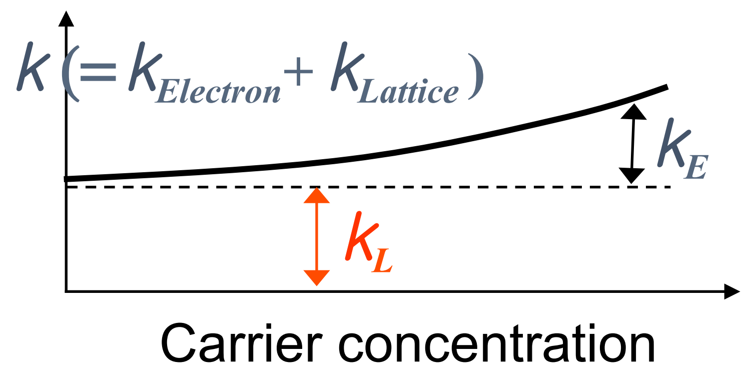
Bismuth Telluride
(low efficiency, low abundance, high cost)

"Any sufficiently advanced technology is indistinguishable from magic." Arthur C. Clarke

Bermuda Triangle of Thermoelectrics

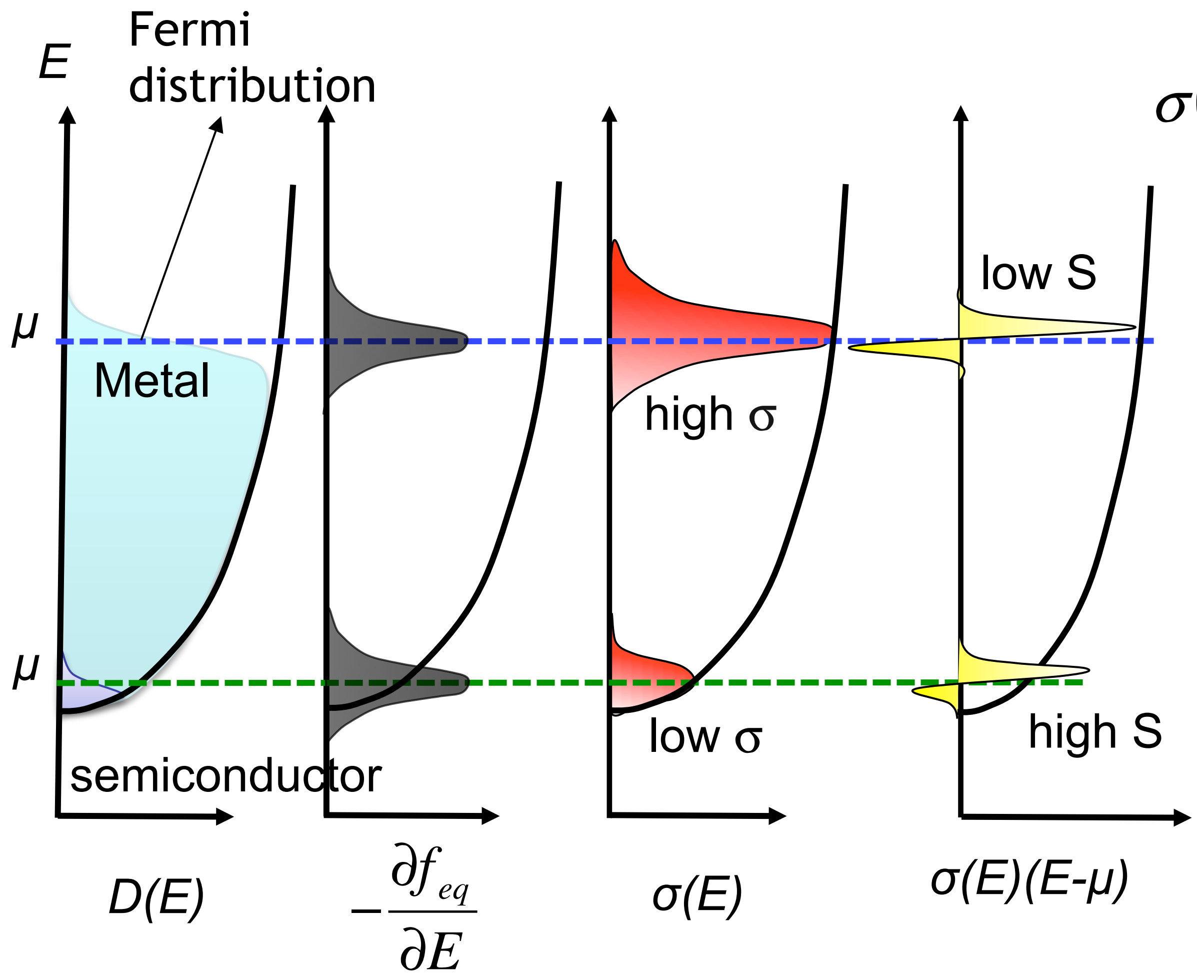






"Any sufficiently advanced technology is indistinguishable from magic." Arthur C. Clarke

Band Picture of Thermoelectric Parameters



Electrical Conductivity, σ

$$\sigma = \int \sigma(E)dE$$

$$\sigma(E) = q^2 D(E)\tau(E)v(E)^2\left(-\frac{\partial f_{eq}}{\partial E}\right)$$

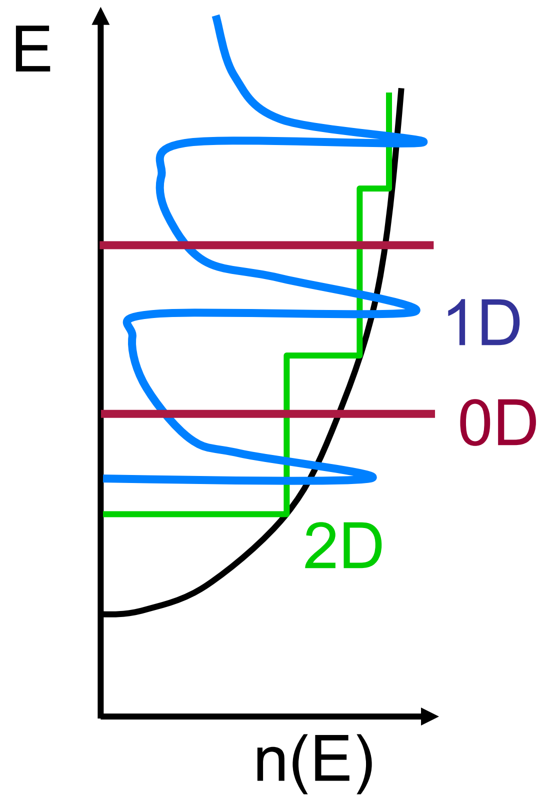
Thermopower, S

$$S = \frac{1}{eT}\frac{\int \sigma(E)(E-\mu)dE}{\int \sigma(E)dE}$$

$$S \sim m^* \sim \frac{1}{\partial^2 E / \partial k^2}$$

ow do we increase $S^2\sigma$

rostructure



5

Quantum
Confinement

(Hicks & Dresselhaus, 1993)

How do we reduce k

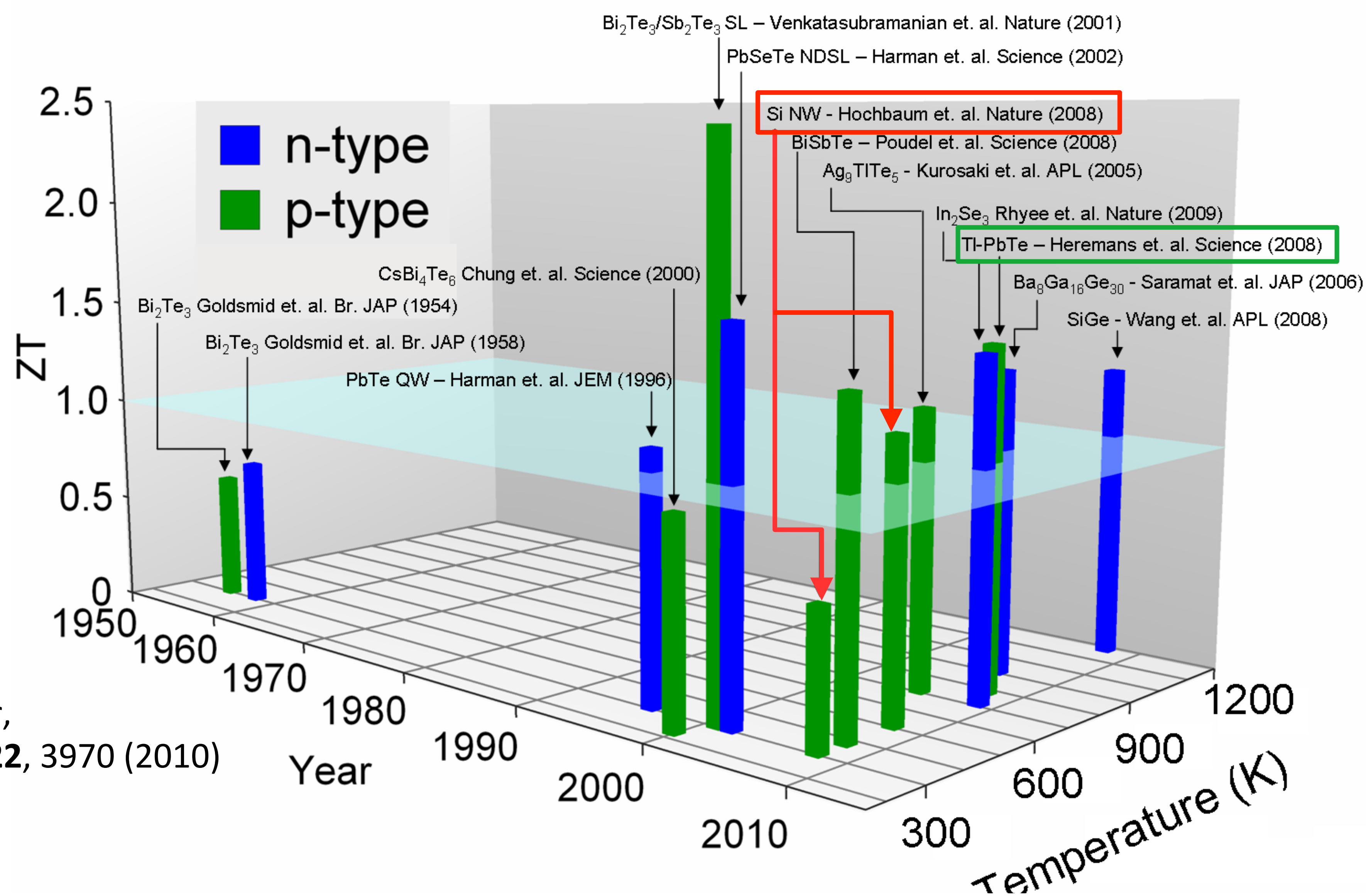
$$k = Cvl/3$$

$C = 2\times10^6\ J/m^3$-K - Dulong-Petit
v = 2000-4000 m/s
l = 0.2-0.5 nm (atomic scale)

k_{min} = 0.25-1 W/m-K

Vineis, Shakouri, Majumdar,
Kanatzidis, *Adv. Materials* **22**, 3970 (20

ZT Map

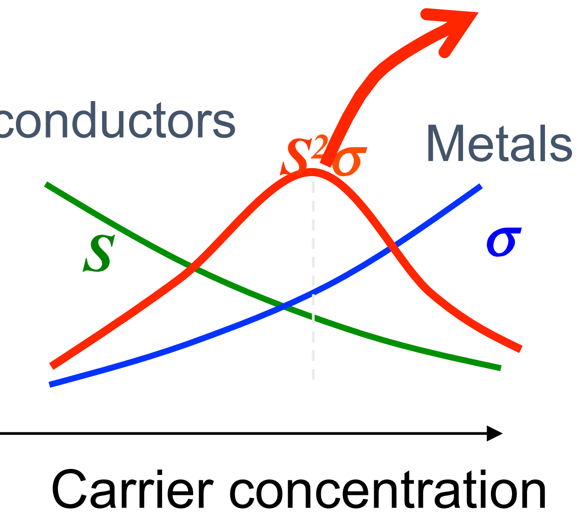


kouri, Majumdar,
, *Adv. Materials* **22**, 3970 (2010)

rd | ENGINEERING
Engineering

Viable Options

...als with large DOS ...k_BTs from E_F



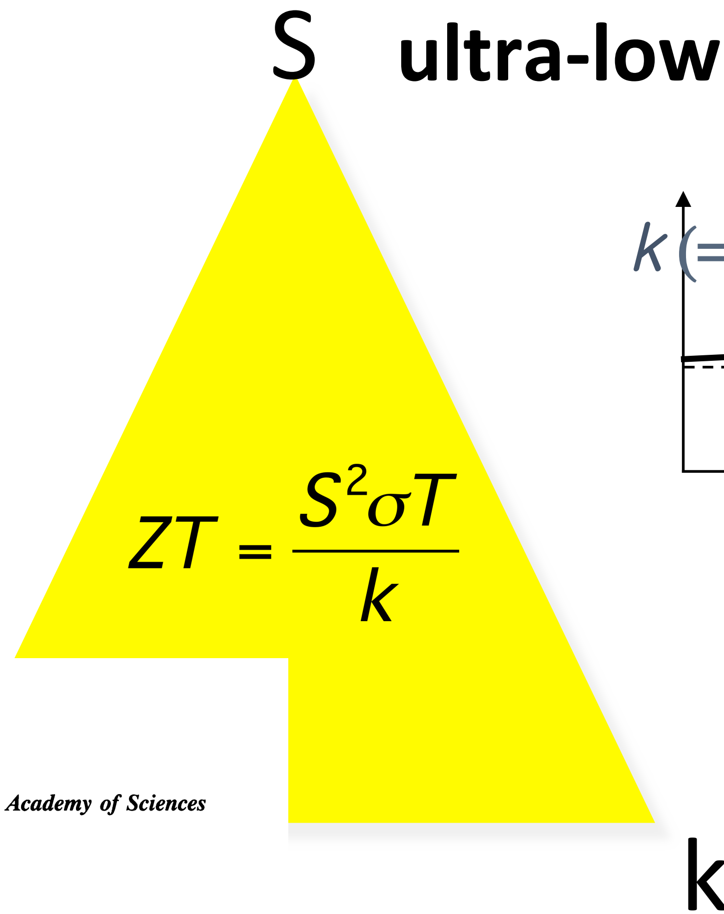
...i. USA
...439, July 1996
...ences

... is part of a special series of Inaugural Articles by members of the National Academy of Sciences
...25, 1995.

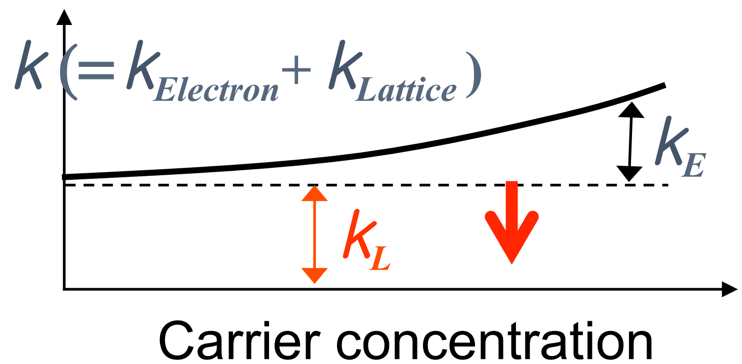
...thermoelectric

... AND J. O. SOFO‡

...s and Astronomy, The University of Tennessee, Knoxville, TN 37996-1200; †Solid State Division, Oak Ridge National Laboratory, P.O. Box
...37831-6030; and ‡Instituto Balseiro, Centro Atomico Bariloche, (8400) Bariloche, Argentina



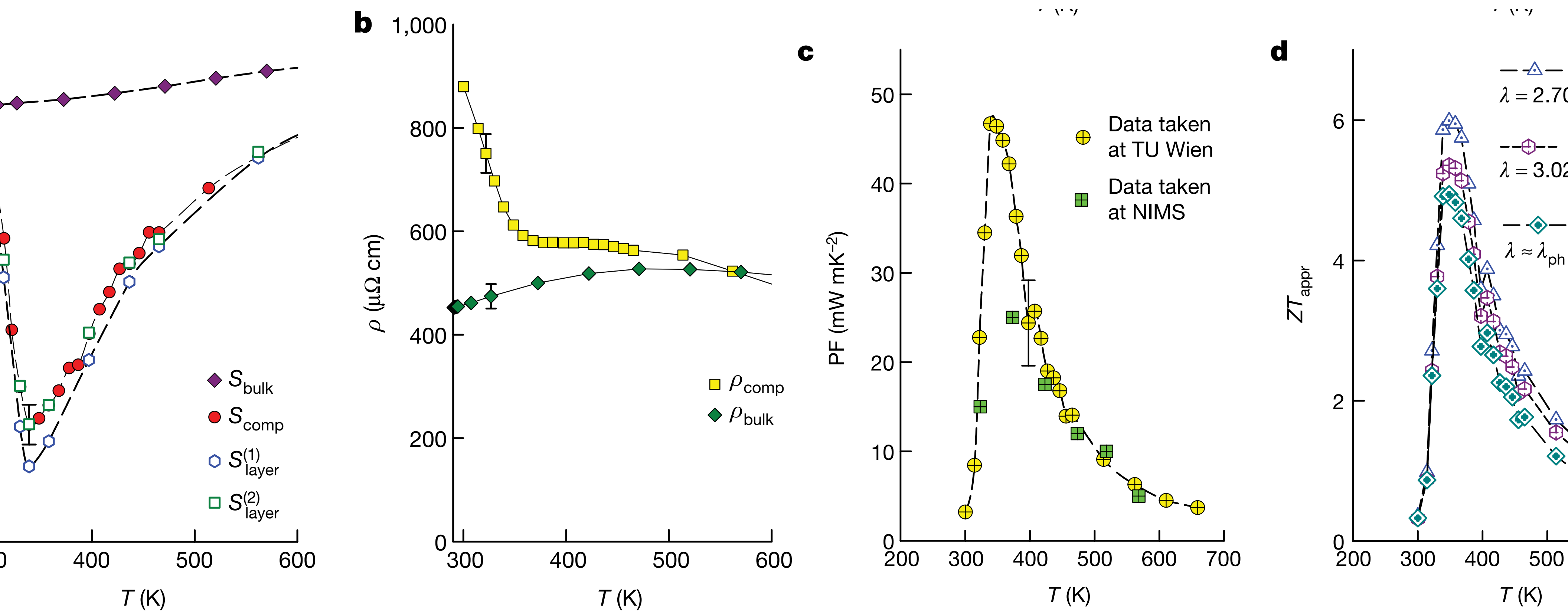
Degenerate Semiconductor... ultra-low k (e.g., localizatio...



$k_{min} < 1$ W/m-K

...nguishable from magic." Arthur C. Clarke

Full-Heusler Alloy



Hinterleitner et al., Nature (2019)

ENGINEERING
Engineering

"Any sufficiently advanced technology is indistinguishable from magic." Arthur C. Clarke

Is there a killer application for thermoelectrics?

r Group

Power Generation from Waste Heat Recovery (100 °C – 800 °C)

Refrigeration & Heat Pumps (10-60 °C)

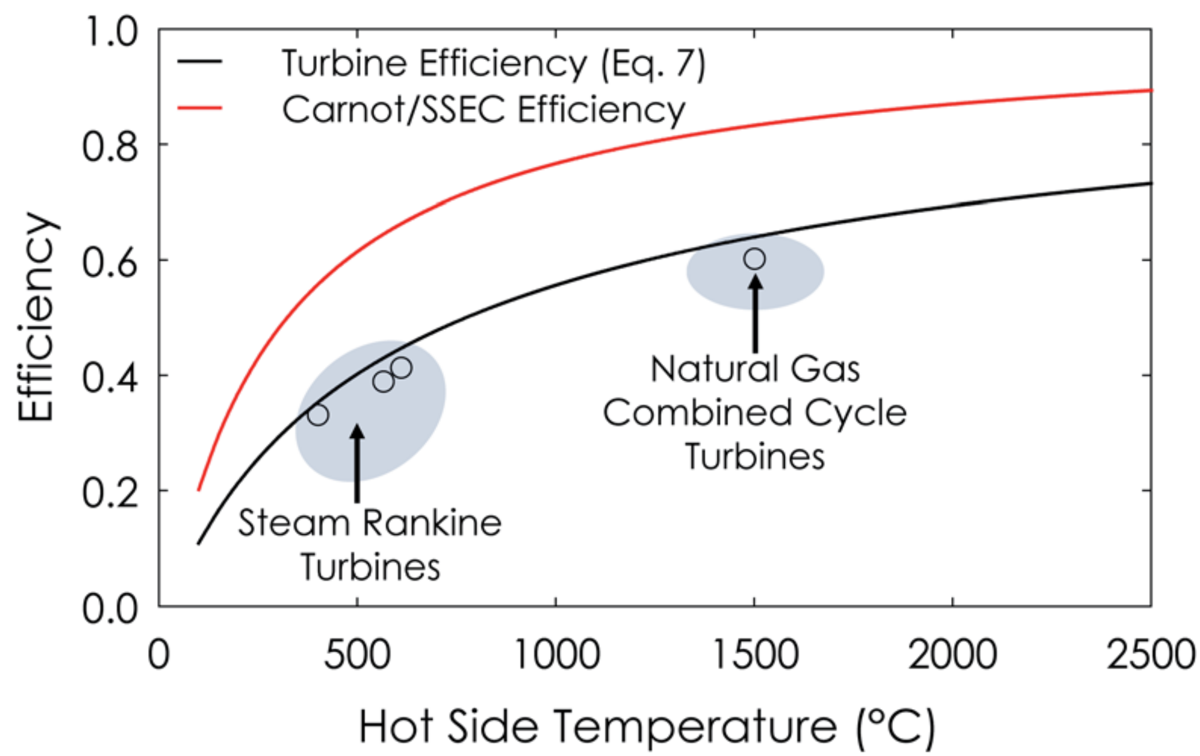
"Any sufficiently advanced technology is indistinguishable from magic." Arthur C. Clarke

Efficiency of Current Heat Engines

$$dW_{max} = dH - T_{amb}dS$$

$$C_P dT \qquad dS = \frac{dQ}{T} = \frac{C_P dT}{T}$$

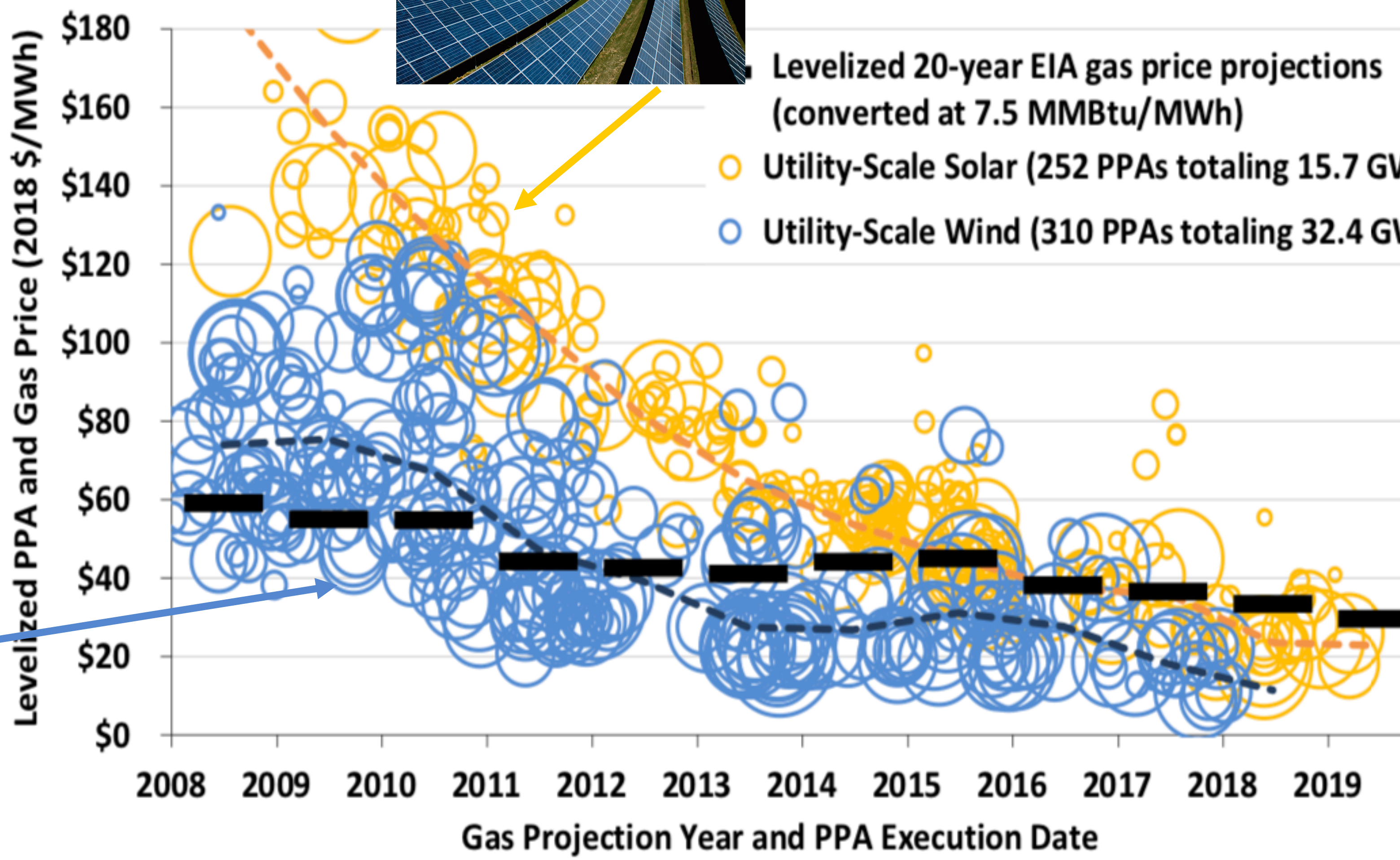
$$\frac{\ldots_{max}}{\ldots Q} = \frac{\int_{T_{amb}}^{T_H} dW_{max}}{\int_{T_{amb}}^{T_H} dQ} = 1 - \frac{T_{amb}}{T_H - T_{amb}} \ln\left(\frac{T_H}{T_{amb}}\right)$$



Henry & Prasher, *Energy & Env. Science* (2014)

r Group

Carbon-Free Power Generation

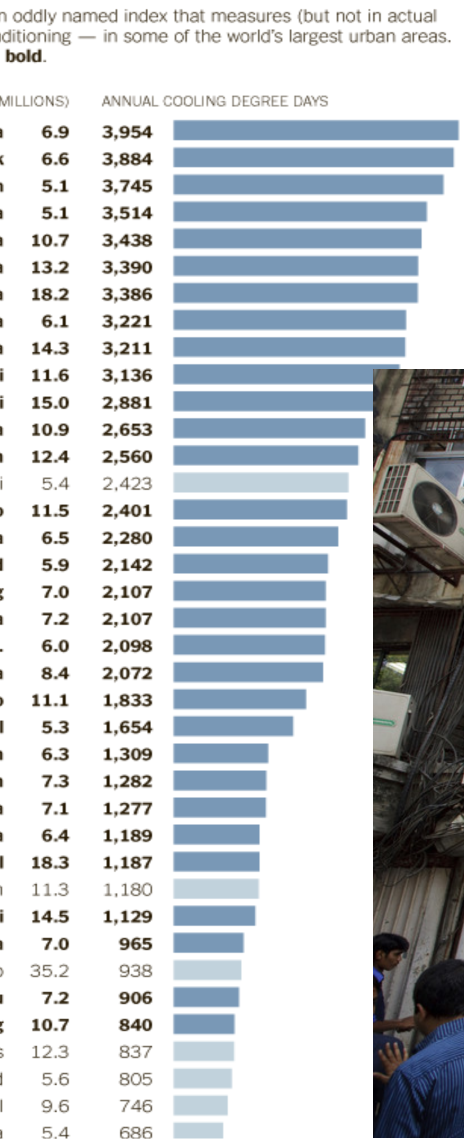


rd | ENGINEERING
Engineering

"Any suffi

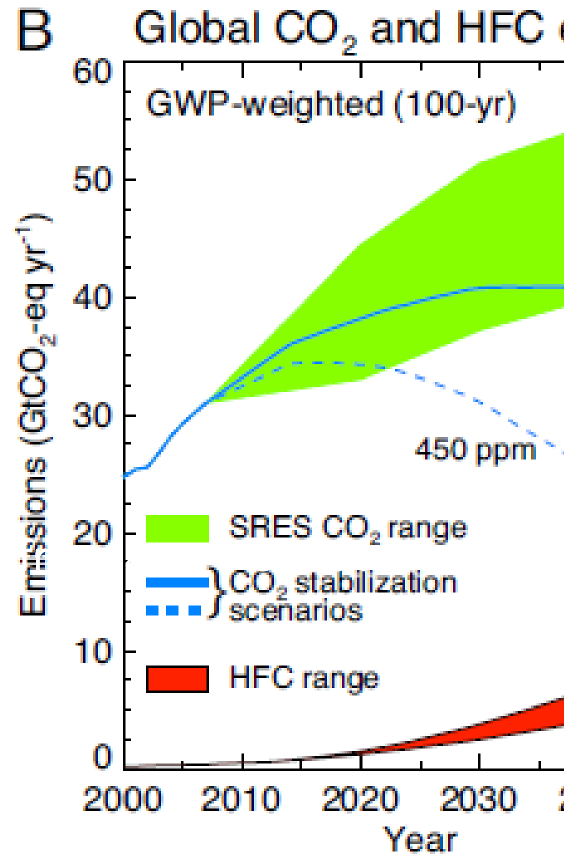
r Group

Global Warming Potential of Refrigerants



Finding the right refrigerant with GWP < 1 is a grand challenge

ke



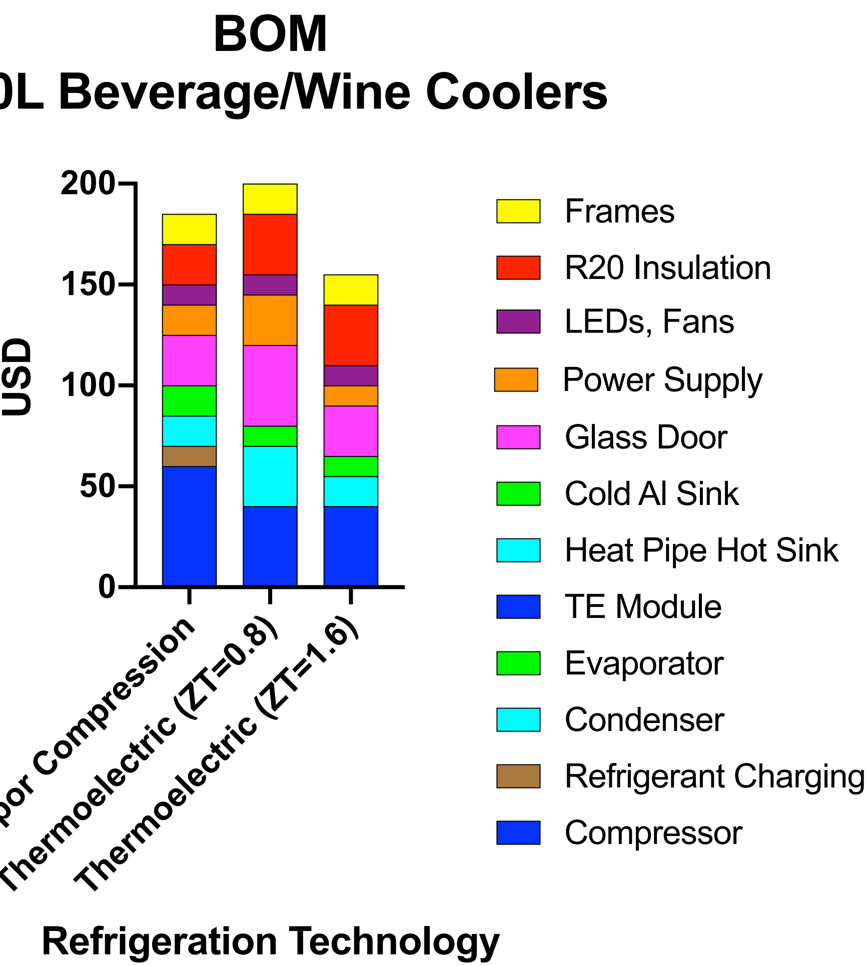
Velders et al., PNAS (200

ACTION FACT SHEET

UNEP

The Kigali Amendment to the Montreal Protocol: HFC Phase-down

Cost Breakdown



True®

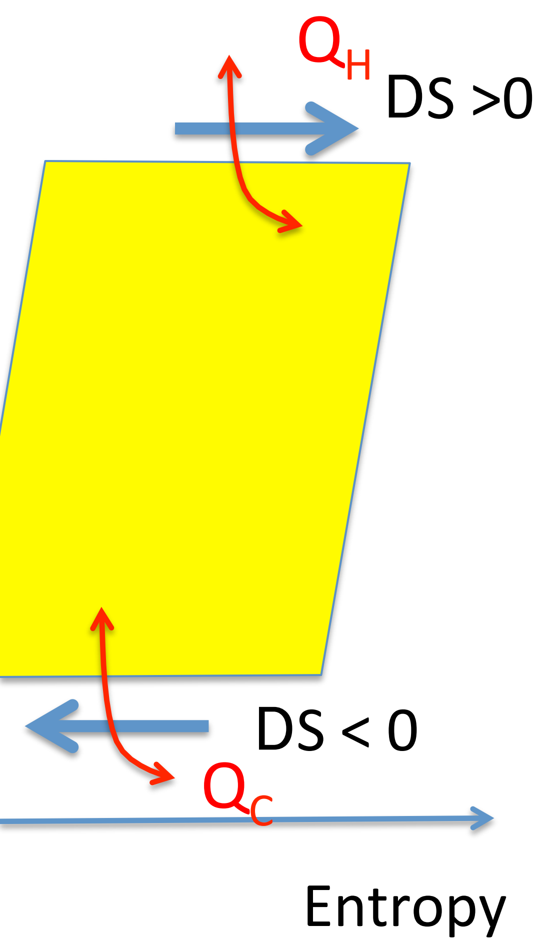
Godrej

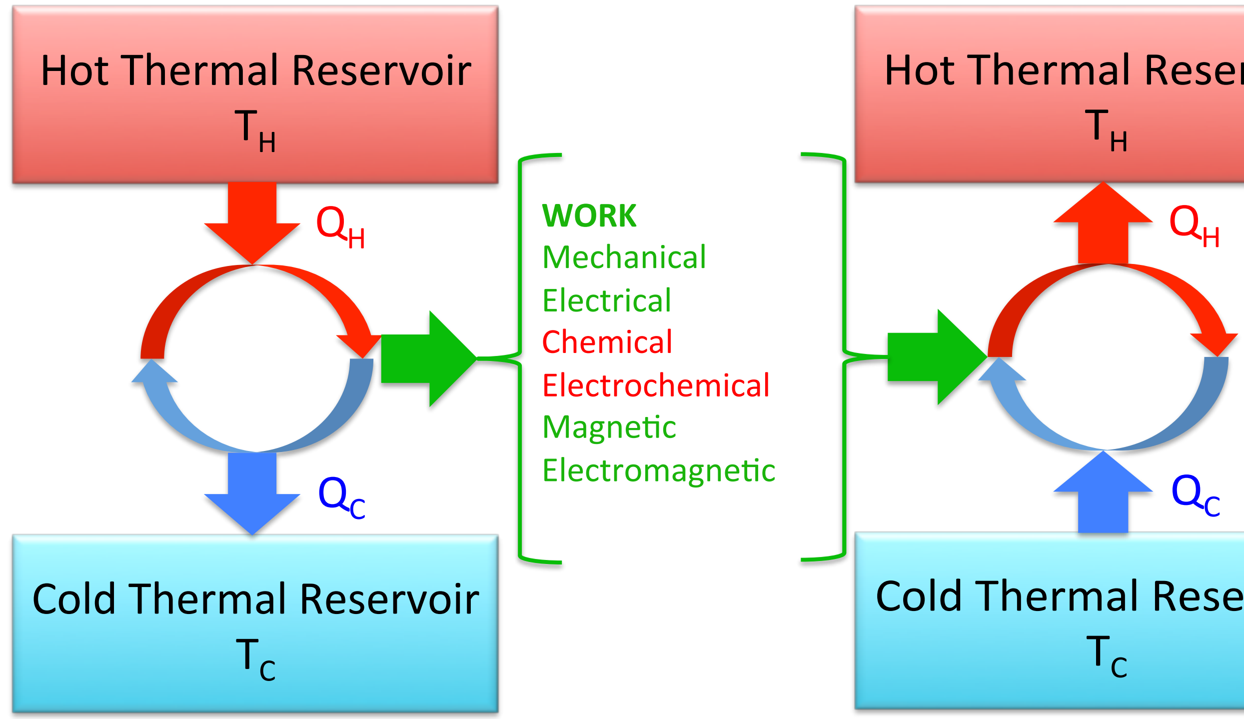
Courtesy: Sheetak Inc.

"Any sufficiently advanced technology is indistinguishable from magic." Arthur C. Clarke

at Engines

er Generation & Cooling





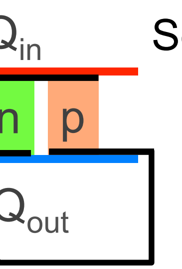
Liquid-Vapor:	**DS, configurational entropy of gas**
Thermoelectric:	**DS, configurational entropy of electrons in**
Electrocaloric:	**DS, orientational entropy of electric dipoles**
Magnetocaloric:	**DS, orientational entropy of magnetic dipo**
Electrochemical:	**DS, entropy of solvent-solute in redox react**
Chemical:	**DS, entropy of oxidizing/reducing medium**

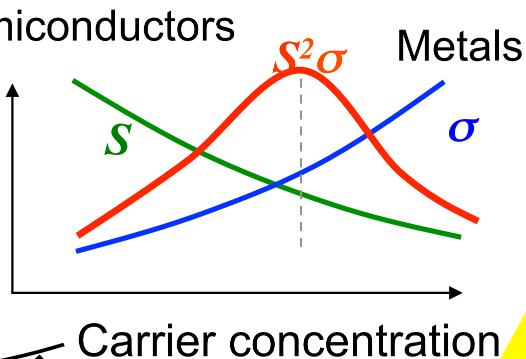
Entropy of Energy Carriers & Excitations

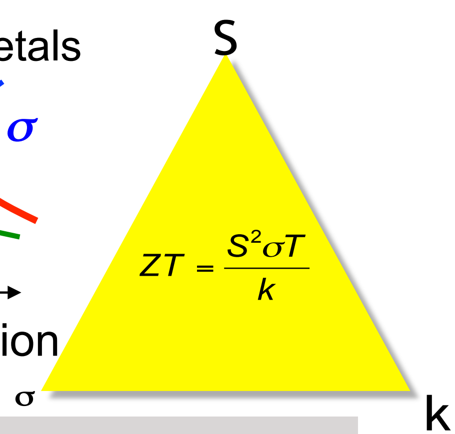
apor: DS, configurational entropy of gas
electric: DS, configurational entropy of electrons in k-space
loric: DS, orientational entropy of electric dipoles
ocaloric: DS, orientational entropy of magnetic dipoles
hemical: DS, entropy of solvent-solute in redox reaction
l: DS, entropy of oxidizing/reducing medium

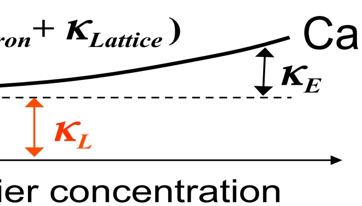
Water Liquid-Vapor:
DS = 6.3 kJ/kg-K ≅ 1.17 mV/K

Is this the theoretical limit fo



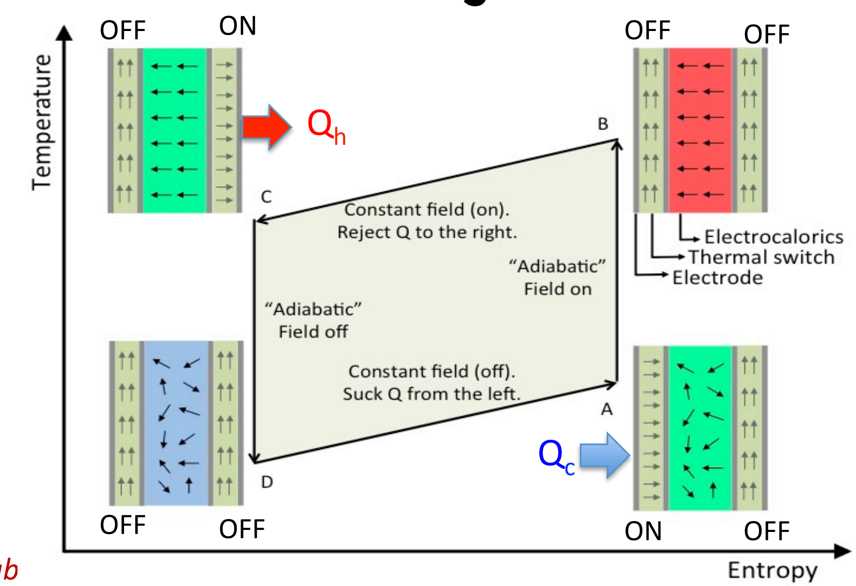






Very hard to decouple S, s, k and improve ZT to 3

Electro/Magnetocaloric



Temp
Sepa
Unip

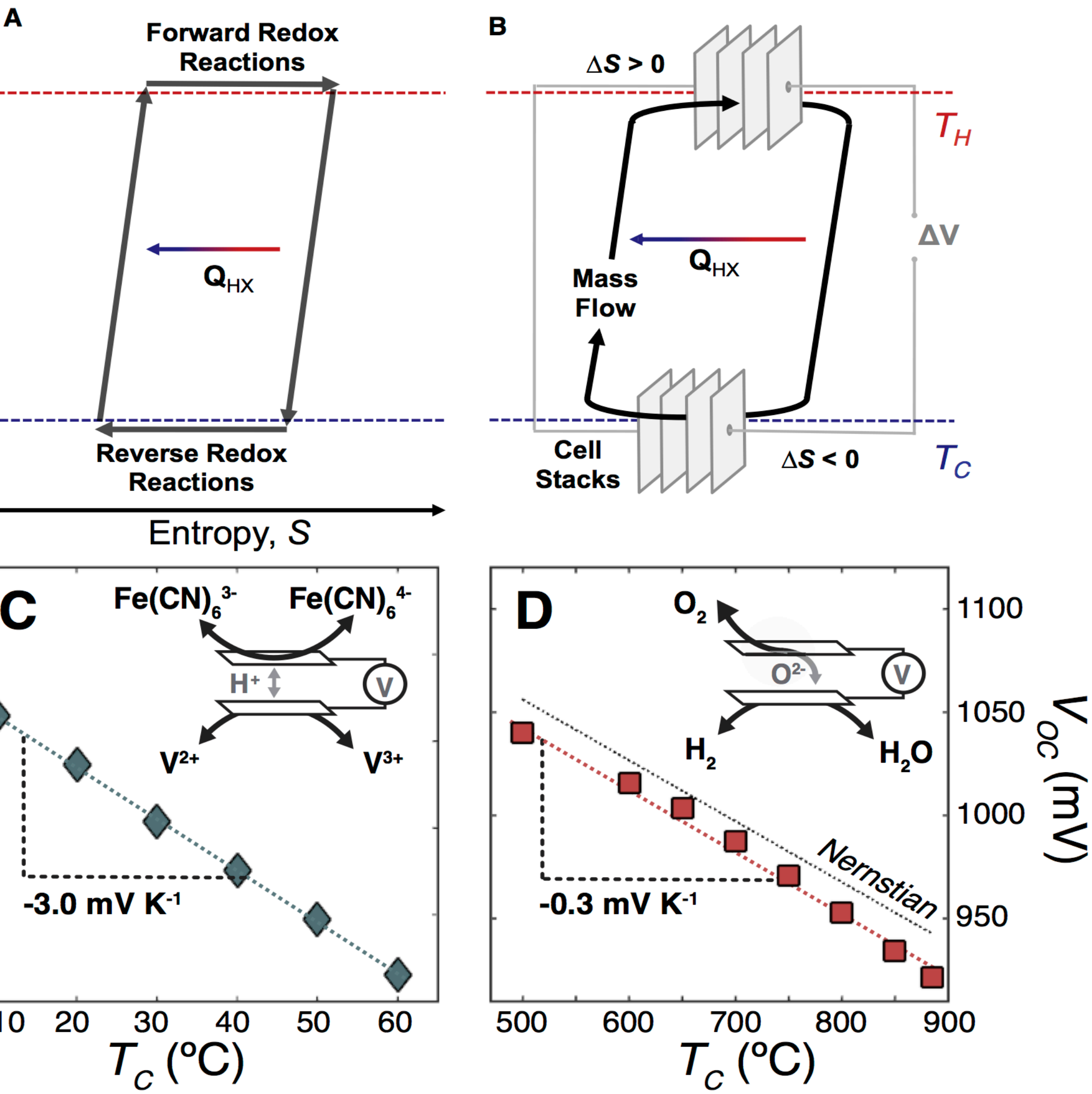
Ther
swit

rd | ENGINEERING
Engineering

"Any sufficiently advanced technology is indistinguishab

r Group

Continuous Electrochemical Heat Engines



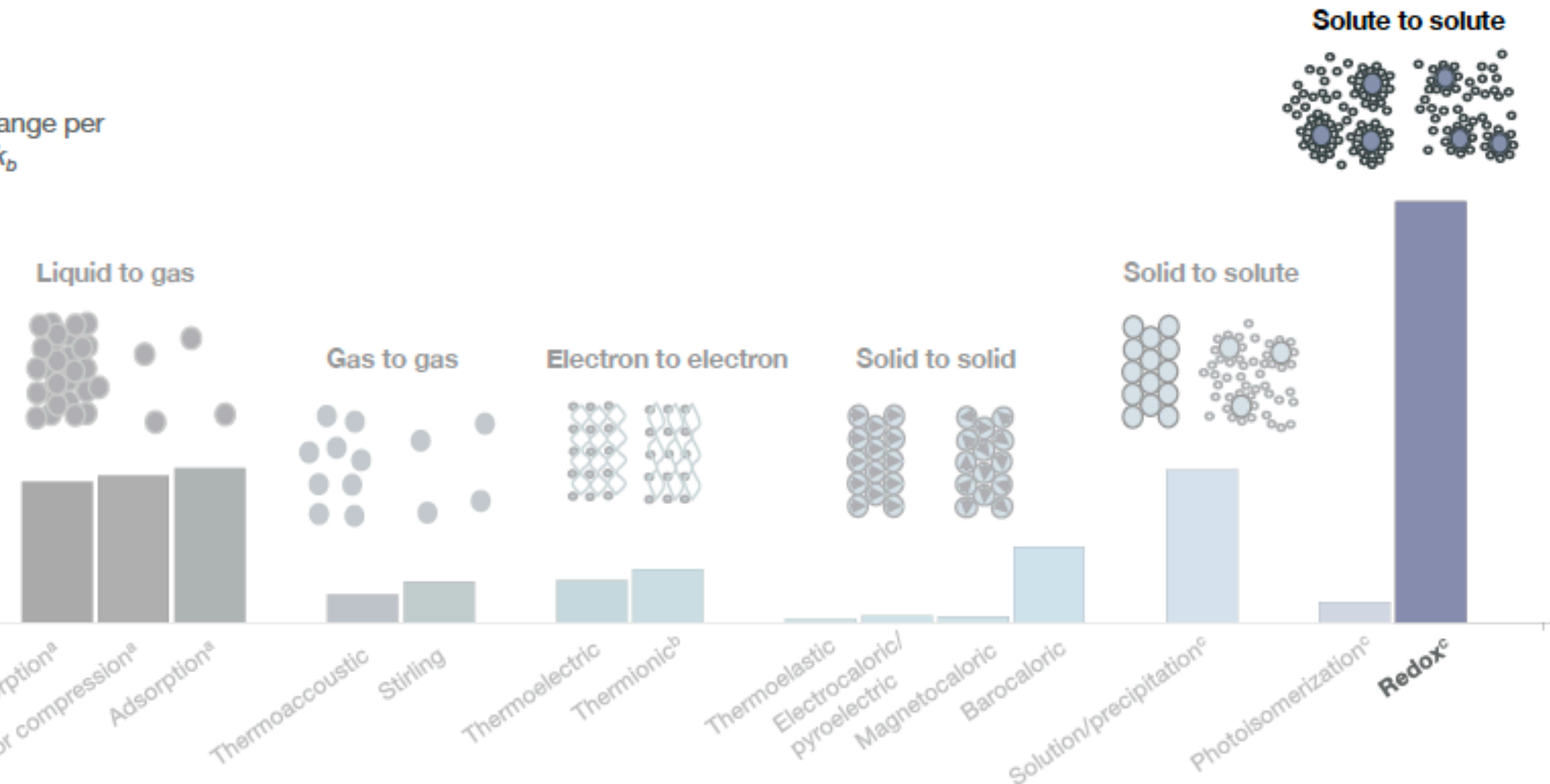
Redox Couple	α (
$Fe(CN)_6^{3-/4-}$	
Methyl viologen (2+/1+)	
$Fe^{2+/3+}$	
$V^{2+/3+}$	

DS > 1.17 mV/K
More than liquid-vapor phase transi

Poletayev, McKay, Chueh, Majumdar, *Energy & Env Sci* (2018)

ble from magic." Arthur C. Clarke

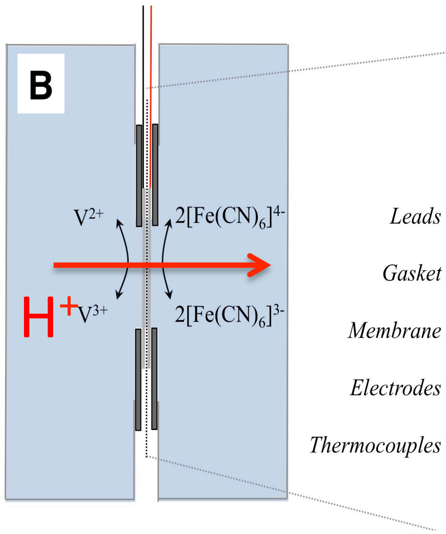
Entropy Changes in Nature

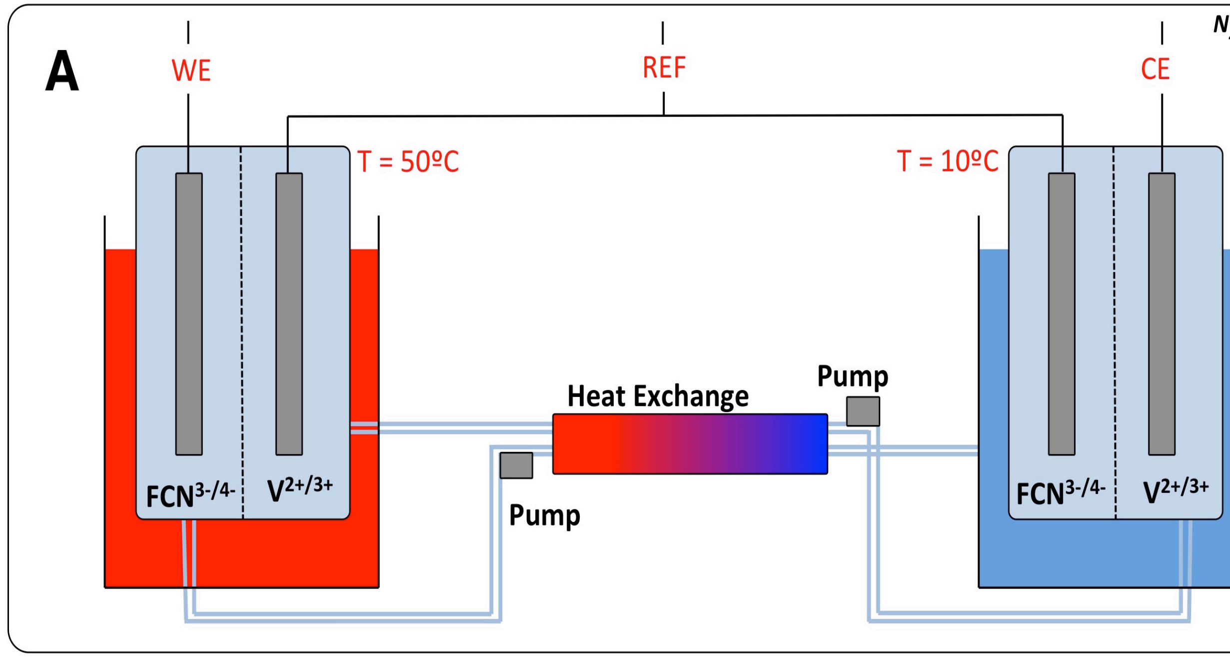


rd | ENGINEERING
Engineering

"Any sufficiently advanced technology is indistinguishable from magic." Arthur C. Clarke

Experimental Set Up





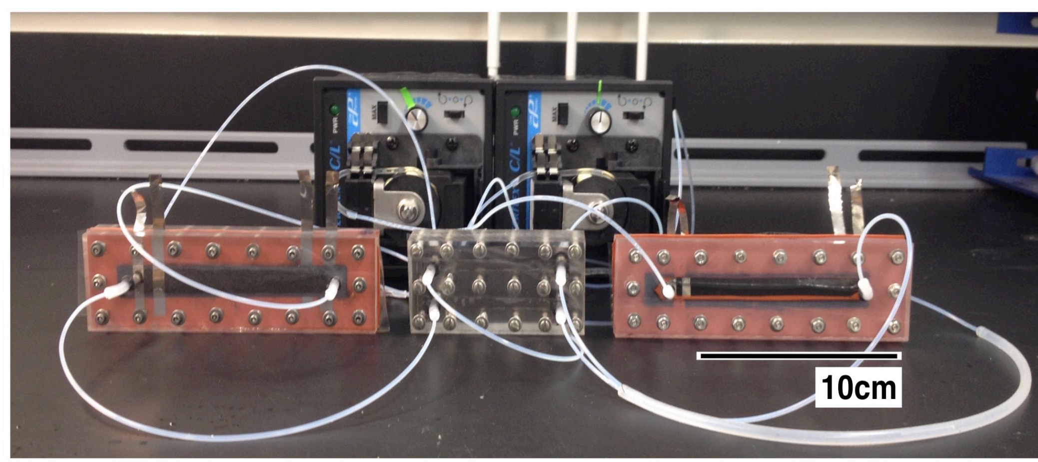
PLING OF TRANSPORT & ENTROPY

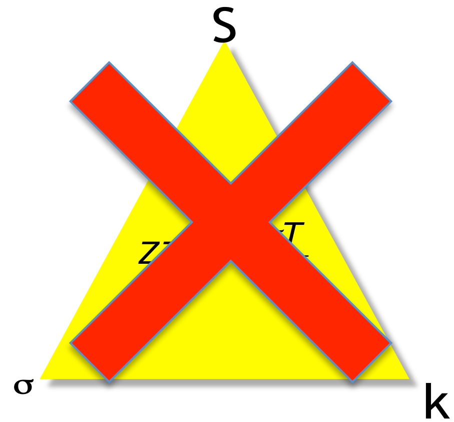
trochemical redox reactions

uctance of proton exchange membrane

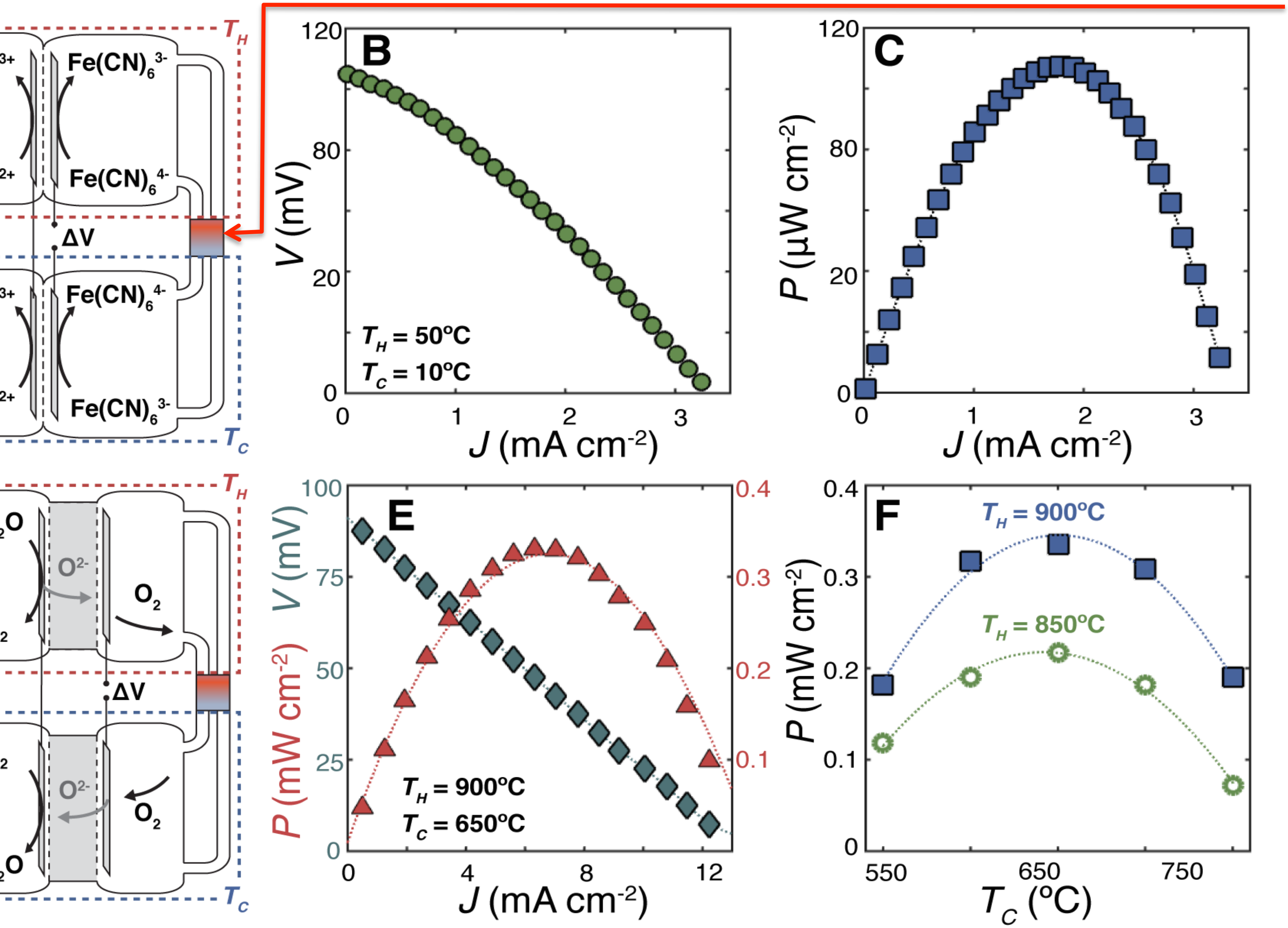
perative heat exchanger

B





Continuous Electrochemical Heat Engines



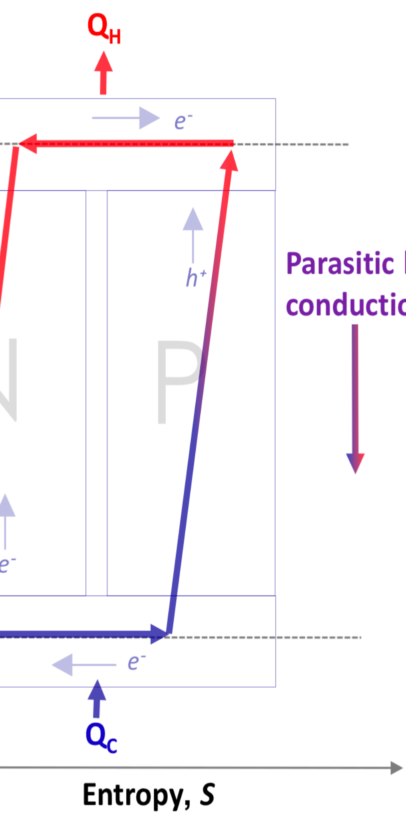
Recuperative
Heat Exchang

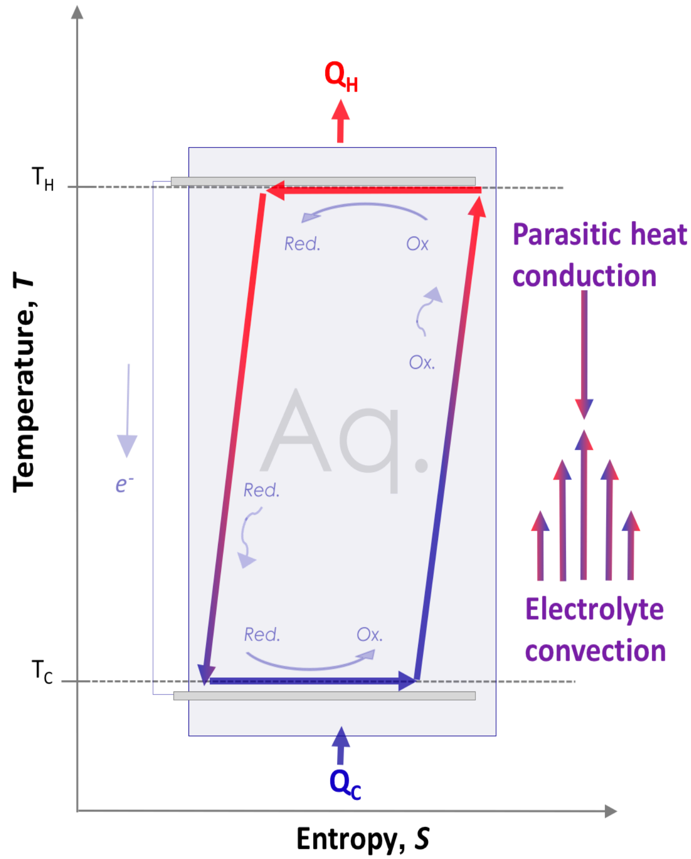
Currently abo
20% of Carno
limit

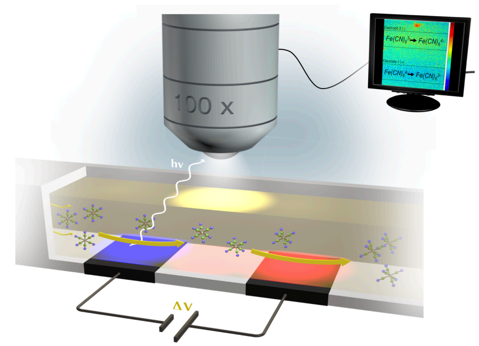
Estimates of
60-70% of
Carnot limit w
better heat
exchangers

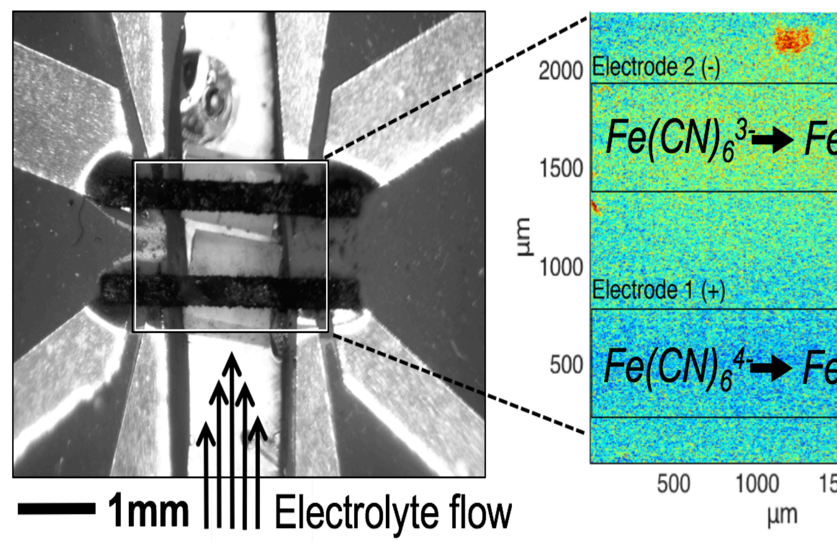
Redox Refrigeration


Ian McKay







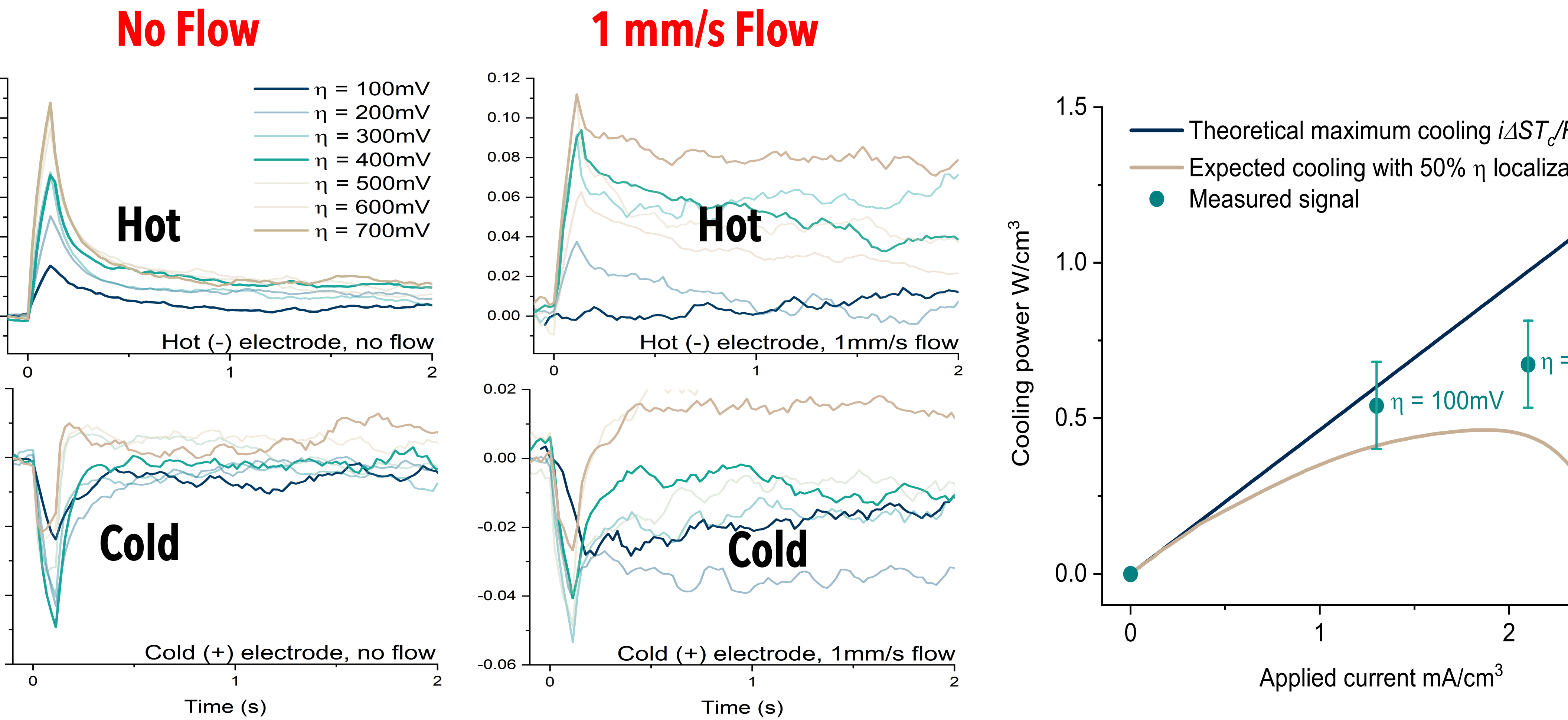


McKay, Kunz, Majumdar, Redox Refrigeration, *Scientific Reports* (2019).

rd | ENGINEERING
Engineering

"Any sufficiently advanced technology is indistinguishable from magic." Arthur C. Clarke

Redox Refrigeration with Flow



"Any sufficiently advanced technology is indistinguishable from magic." Arthur C. Clarke

Classification of Redox Refrigerants

r Group

$=[\Delta S(J/mol\cdot K)T(K) - E\downarrow a\ (J/mol)]\times C(mol/kg)/c\downarrow p\ (J/kg\cdot K)$

ble Thermodynamics

$/mol\cdot K)\cdot C(mol/kg)/c\downarrow p\ (J/$

$YT = DT_{max}$

s

$=\Delta S(J/mol\cdot K)T(K)/E\downarrow a\ (J/mol)$;

> 1

Redox reaction	α, mV/K	YT= ΔT_{max} @300K, K	$Q_{g/b}$ (
$2H^+ + 2e^- \rightarrow H_2(g)$	0.8	307	4.0[9,2
$V^{3+} + e^- \rightarrow V^{2+}$	1.2-1.9*	36	6.0[27
$V^{5+} + e^- \rightarrow V^{4+}$	-0.2*	6	2.4[27
$Br_2(l) + e^- \rightarrow 2Br^-$	0.3*	14	1.7[28
$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}$	-1.5*	10.6	78.4
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	1.1*	36	95.7
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	2.2	7	219.
$Ce^{5+} + e^- \rightarrow Ce^{4+}$	2.3	13	36.0
$S_2^{2-} + 2e^- \rightarrow 2S^{2-}$	-.7	9.4	1.3[9,3

Is there a killer application for thermoelectrics?

Power Generation from Waste Heat Recovery (100 °C – 800 °C)

Refrigeration & Heat Pumps (10-60 °C)

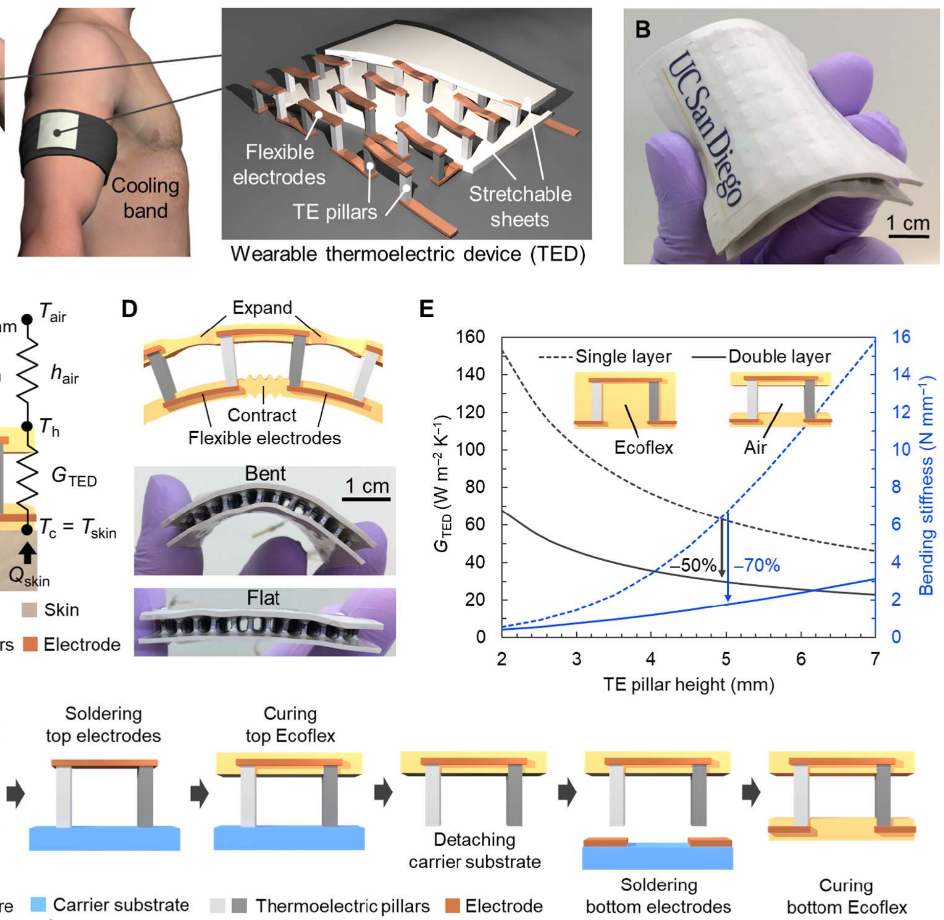
"Any sufficiently advanced technology is indistinguishable from magic." Arthur C. Clarke

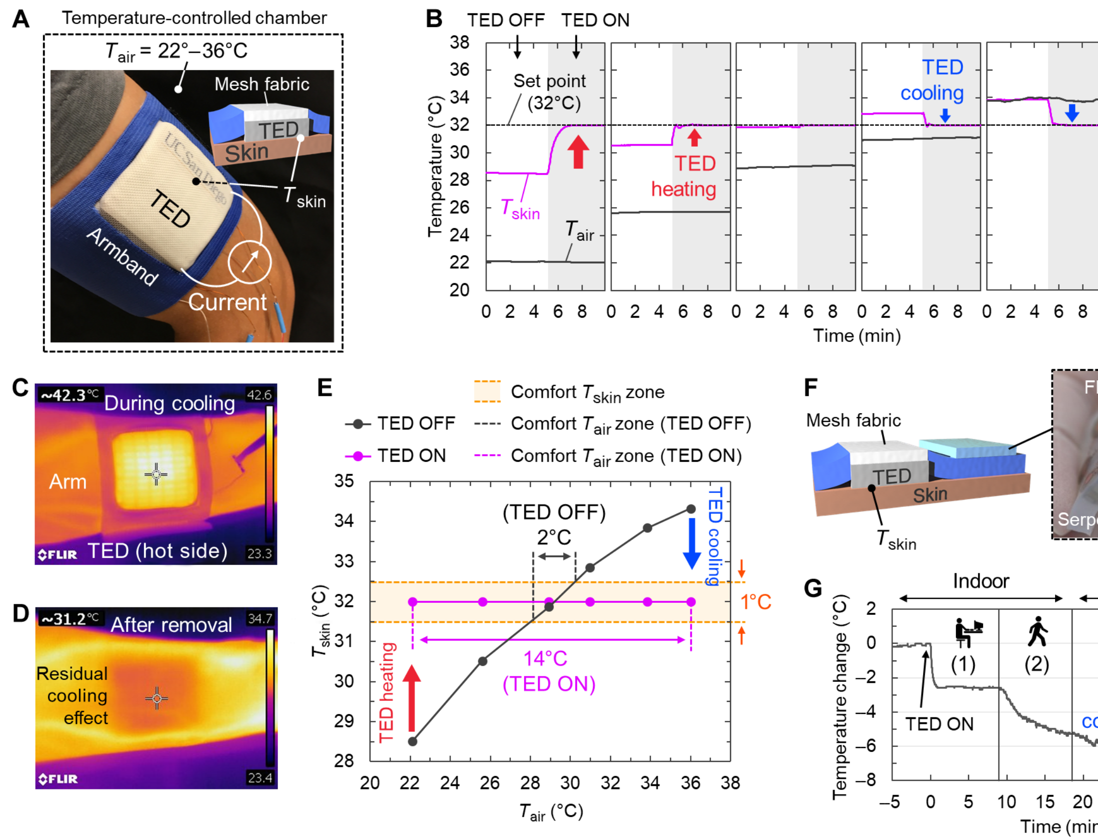
SCIENCE ADVANCES | RESEARCH ARTICLE

ENGINEERING

Wearable thermoelectrics for personalized thermoregulation

Sahngki Hong[1,2], Yue Gu[1,3], Joon Kyo Seo[1,3], Joseph Wang[1,3], Ping Liu[1,3], Y. Shirley Meng[1,3,4], Sheng Xu[1,3]*, Renkun Chen[1,2,4]*





ENGINEERING
Engineering

"Any sufficiently advanced technology is indistinguishable from magic." Arthur C. Clarke