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Pyroelectrically-driven chemical reactions described by a novel thermodynamic cycle – **Supplementary Information**

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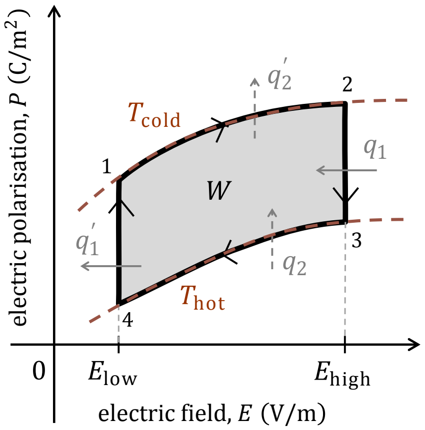
S1 Olsen and Resistive Cycles

The Olsen Cycle (Fig. S1a) comprises four steps in which the polarisation of the pyroelectric is varied in an externally applied electric field between two different temperatures. Starting at point 1, the polarisation of the material is intensified at constant low temperature by increasing the external electric field to E_{high}. In the process, heat (q_2') is lost to the cold reservoir as a consequence of entropy reduction. From point 2, the temperature is increased to T_{hot} at constant E_{high}, which leads to a polarisation reduction in the pyroelectric. Along the line 3→4 the applied electric field is diminished at constant (hot) temperature, so that the material is further discharged. At the same time, the pyroelectric takes up heat from the hot reservoir (q_2). From point 4 charging restarts by cooling the pyroelectric to T_{cold} at constant electric field E_{low}.

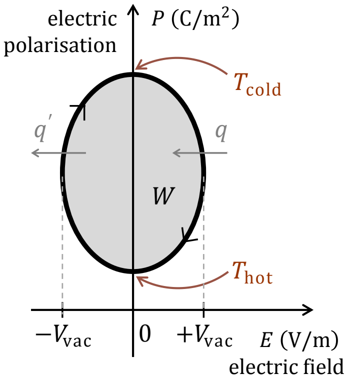
The expression for the efficiency of the Olsen cycle yields lower values than that for the Carnot cycle, as there are two and not just one process steps with heat extraction from a hot source. If a heat regenerator is integrated which reuses the heat extracted from the pyroelectric in step 4→1, the efficiency comes close to that of the Carnot process.[1]

For some applications, it is not possible or necessary to apply an electric field together with temperature variations. By attaching a load resistor to the pyroelectric, the surface charges on it are delayed from short-circuiting, thus accumulating and giving rise to an induced electric field, which is the cause for the area in the *PE*-diagram in Fig. S1b. This mode of operation is called *the resistive cycle*. Even though its area is not as large as that in Fig. S1a, it shows that temperature variations alone – with no external electric field – still allow for the extraction of electrical work.

Although it was demonstrated that around a hundred times more energy can be gained from operation with the Olsen cycle,[2] most researchers have used the resistive cycle as it is simpler to implement.



(a) Olsen cycle



(b) Resistive cycle

Fig. S1 Pyroelectric cycles for the extraction of work from temperature variations. (a) The Olsen cycle consists of 1→2: isothermal charging, 2→3: heating at constant electric field, 3→4: isothermal discharging and 4→1: cooling at constant field. q_1, q_2: heat entering the system; q_1', q_2': heat leaving the system; W: extractable work. (b) The resistive cycle for the extraction of work from temperature variations without an external electric field. q, q': heat entering/leaving the system, respectively; W: extractable work; V_{vac}: maximum voltage for a given temperature difference in vacuum.

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S2 Calculation of the Overpotential

Subject of this section is the choice for $V_n = 1.48\,\mathrm{V}$ instead of $E = 1.23\,\mathrm{V}$ for the overpotential. The starting point is eqn S1, which describes total entropy changes as the sum of the system and its surroundings. By multiplying it with $-T$, we get to eqn S2, where the quantities $-T\Delta S_{\mathrm{universe}}$ and $-T\Delta S_{\mathrm{surroundings}}$ are given the names ΔG and ΔH respectively (eqn S3). In this way, the significance of a negative sign for ΔG in spontaneous reactions becomes apparent as the need for the total entropy to increase – the driver for chemical reactions. The heat absorbed or emitted by the system ΔH must be taken from or given away to the surroundings, thus decreasing (or increasing) their entropy.

$$\Delta S_{\mathrm{universe}} = \Delta S_{\mathrm{surroundings}} + \Delta S_{\mathrm{system}} \quad \text{(S1)}$$

$$-T\Delta S_{\mathrm{universe}} = -T\Delta S_{\mathrm{surroundings}} - T\Delta S_{\mathrm{system}} \quad \text{(S2)}$$

$$\Delta G = \Delta H - T\Delta S \quad \text{(S3)}$$

$$\Delta H = \Delta G + T\Delta S \quad \text{(S4)}$$

The reaction of interest is the hydrolysis of water (eqn S5). In this reaction, ΔH is very positive (285.8 kJ/mol at 25 °C) and so is ΔS (163.3 J/K mol), as 1.5 mol of gases are produced from a single molecule in the liquid state. ΔG (237.1 kJ/mol) is therefore positive (non-spontaneous) at temperatures lower than about 700 °C.

$$\mathrm{H_2O(l)} \xrightarrow{\mathit{energy}} \mathrm{H_2(g)} + \frac{1}{2}\mathrm{O_2(g)}, \qquad E^\circ = \frac{\Delta G^\circ}{-nF} = 1.23\,\mathrm{V} \quad \text{(S5)}$$

$$V_n = \frac{\Delta H}{-nF} = 1.48\,\mathrm{V} \quad \text{(S6)}$$

The minimum amount of energy required to drive the reaction is given by ΔG. If this energy is provided by an electric potential, the potential must be equal or greater than $E^\circ = 1.23\,\mathrm{V}$. Thus, 1.23 V is the absolute minimum potential. However, if electrolysis is carried out under such conditions, the system will have to withdraw heat from the surroundings (and increase its entropy) in order to be able to expand the volume of the gaseous products.

Another possibility is to provide the total energy – both for reaction and for expansion (eqn S4). In this operation mode, no additional heat has to be withdrawn from the surroundings. The required voltage is called the thermoneutral potential $V_n = 1.48\,\mathrm{V}$ at 25 °C (eqn S6).

Now let us come back to the pyroelectric system shown in Fig. 2. Water electrolysis does not take place at constant temperature but while cycling the pyroelectric. Perhaps it would be possible to operate pyroelectrolysis at 1.23 V during the heating phase of the cycle, since the additional entropy energy would be provided. However, reactions would be prohibited during the cooling phase. This is the reason why a minimum potential of V_n is assumed to be mandatory.

On the other hand the required bending of electronic bands – the predicted necessary (threshold) reaction potential V_{th} – will be considerably higher than V_n, so that the expansion energy will already be provided. Under this condition we can continue with $E = 1.23\,\mathrm{V}$.

S3 Calculated Pyroelectrochemical Yields

Table S1 shows input numbers used for the pyroelectrocatalytic simulation as well as simulated outputs. Whenever material parameters were provided by authors, these numbers were taken. Else, they were obtained from further literature. The pyroelectric coefficient and permittivity for $\mathrm{BaTiO_3}$ are temperature dependent and are displayed in Fig. S2a and S2b.

The calculated value $\eta_{\mathrm{H_2,max}} > 1$ for phosphorene is a result of the dataset used. The reported pyroelectric coefficient for black phosphorene is extremely high.[3] However, no data was found for its relative permittivity so that the permittivity value of bulk phosphorous was taken. This permittivity is one order of magnitude lower than for perovskites.

As discussed in the main text, the density states at the surface of the pyroelectric determine how large the surface band gap E_g' will be. It may take values from 0 to the full bulk E_g, thus largely influencing the threshold efficiency and hydrogen yield. Simulation outputs for some relevant E_g' are shown in Table S2.

Tabelle S1 Input and output simulation values (used for values in Tab. 2 in the main document)

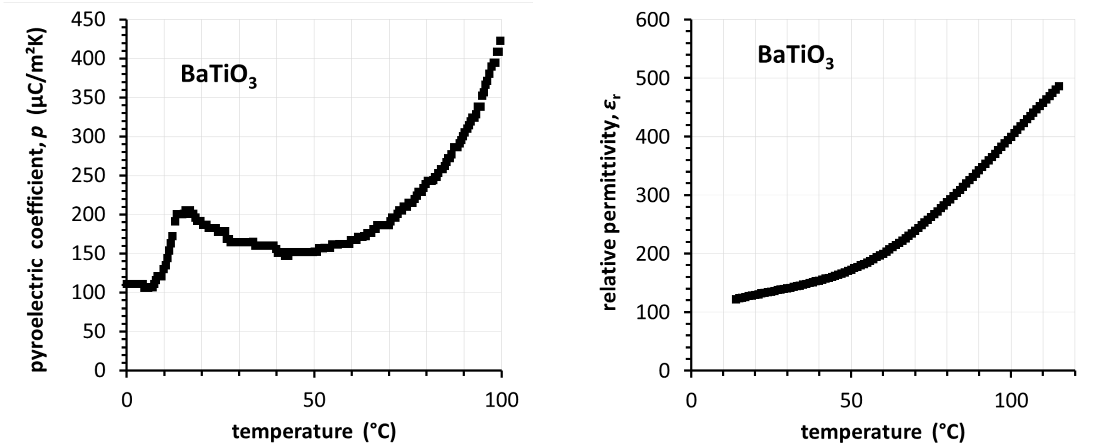
parameter	unit	**phosphorene**	**$Ba_{0.7}Sr_{0.3}TiO_3$**	**$BaTiO_3$**
		MATERIAL PROPERTIES		
$\bar{p}$	μC/m^{2}K	5287[3]	1560[4]	165[5]
E'_g	eV	0.6	0.25	3.08
ρ	kg/m^{3}3	2340	6020	6020
$\bar{\varepsilon}_r$	–	2.82[3]	5.76×10^3[4]	191
c_P	J/kgK	770	527[6]	527[6]
		OPERATIONAL PARAMETERS		
m	mg	1.0	10	3.10×10^3
T_{cold}	K	15	25	40
T_{hot}	K	65	50	70
$2t_e$	s	600	600	120
		MATERIAL DIMENSIONS		
a (thickness)	m	1.0×10^{-6}[a]	2.0×10^{-7}	8.0×10^{-5}
volume	m^3	3.5×10^{-22}	8.0×10^{-21}	5.12×10^{-13}
$N_{particles}$	–	1.2×10^{12}	2.1×10^{11}	1.0×10^6
A	m^2	1.22	8.3×10^{-3}	6.4×10^{-3}
		PTC QUANTITIES		
q_{in}	J	0.0385	0.132	49
V_{vac}	V	3.7	0.149	235
V_{th}	V	1.83	1.48	4.31
Q_{tot}	C	2.64×10^{-13}	1.56×10^{-15}	3.13×10^{-11}
Q_{rx}	C	2.92×10^{-15}	0	3.01×10^{-11}
E_{th}	V/m	5.23×10^9	7.4×10^6	5.39×10^4
		KEY QUANTITIES		
a_{crit}	m	3.46×10^{-10}	3.98×10^{-6}	2.93×10^{-6}
a_{opt}	m	6.92×10^{-10}	7.96×10^{-6}	5.86×10^{-6}
ΔT_{crit}	°C	49.5	498	1.1
FoM	–	2.09×10^1	3.04×10^{-4}	4.29×10^{-5}
		EFFICIENCY FACTORS		
η_{th}	–	0.0111	0	0.963
η_{op}	–	0.672	0.831	0.285
η_F	–	1	1	1
η_{chem}	–	0.00743	0	0.275
		EFFICIENCIES		
η_{pc}[b]	–	0.339	0	5.32×10^{-6}
η_{H_2}	–	0.228	0	1.52×10^{-6}
$\eta_{H_2,max}$	–	2.61[c]	3.80×10^{-5}	5.37×10^{-6}
		HYDROGEN YIELD		
n_{H_2}	mol/g	2.49×10^{-8}	0	5.78×10^{-11}

[a]: These particles are not cuboid but planes with side length 1.0×10^{-6} m. [b]: efficiency of thermal-to-pyroelectric energy conversion according to eqn 9 from the main document. [c]: see Section S3 for an explanation.

Tabelle S2 Surface band gap (E'_g) influence on simulation outputs

	unit	**phosphorene**			**$Ba_{0.7}Sr_{0.3}TiO_3$**			**$BaTiO_3$**		
E'_g	eV	0.3	0.5	0.7	0	1.54	3.08	0	0.25	1.54
V_{th}	V	1.53	1.73	1.93	1.23	2.77	4.31	1.23	1.48	2.77
η_{th}	–	0.173	0.065	0	0	0	0	0.989	0.987	0.976
η_{op}	–	0.804	0.711	0.637	1	0.444	0.285	1	0.831	0.444
n_{H_2}	mol/g	4.66×10^{-7}	1.55×10^{-7}	0	0	0	0	3.22×10^{-10}	2.67×10^{-10}	1.41×10^{-10}

S4 Courses of Pyroelectric Coefficients and Permittivities as a Function of Temperature



(a) p of BaTiO$_3$, taken from Perls *et al.* [5] **(b)** ε_r of BaTiO$_3$, extrapolated from three values by Srinivasan [7]

Fig. S2 BaTiO$_3$ material parameters as a function of temperature.

S5 Python Simulation Code

```
def get_pyro(Ts,pyrofile):  # 1D-array of temperatures, filename of listed pyrocoeff. (T, pyro)
pyros = loadtxt(pyrofile).T  # pyrocoeff. from file
pyro_T  = zeros(len(Ts))  # pyrocoeff. for Ts list of temps
for k in arange(len(Ts)):  # loop over temperatures from given array
for i in arange(len(pyros[0])-1):  # determination of pyrocoeff. for given temp
if pyros[0][i]<=Ts[k] and pyros[0][i+1]>Ts[k]:
pyro_T[k] = pyros[1][i]+(pyros[1][i+1]-pyros[1][i])/(pyros[0][i+1]-pyros[0][i])*(Ts[k]-pyros[0][i])
print "Pyrokoefficient for T = " + str(Ts[k]) + ": " + str(pyro_T[k])
return pyro_T  # 1D-array of pyrocoeff. for Ts input temperature array

def get_epsilon(Ts,epsilonfile):  # 1D-array of temperatures, filename of listed pyrocoeff. (T, pyro)
epsilons = loadtxt(epsilonfile).T  # pyrocoeff. from file
epsilon_T  = zeros(len(Ts))  # pyrocoeff. for Ts list of temps
for k in arange(len(Ts)):  # loop over temperatures from given array
for i in arange(len(epsilons[0])-1):  # determination of pyrocoeff. for given temp
if epsilons[0][i]<=Ts[k] and epsilons[0][i+1]>Ts[k]: epsilon_T[k] = epsilons[1][i]
+(epsilons[1][i+1]-epsilons[1][i])/(epsilons[0][i+1]-epsilons[0][i])*(Ts[k]-epsilons[0][i])
print "Epsilon for T = " + str(Ts[k]) + ": " + str(epsilon_T[k])
return epsilon_T # 1D-array of pyrocoeff. for Ts input temperature array

pyrocoeff = "C:BaTiO3-pyro-Perls1958.txt"  # file for listed pyrocoeff. in muC/(m^2 K)
epsilon = "C:BaTiO3-epsilon-Srinivasan84.txt"
density = 6020.  # kg/m^3 BTO
Egap = 3.08  # full band gap in eV
#Egap = 3.08 / 2.  # band gap in eV, if half of it is taken
#Egap = 0.25  # band gap in eV, a value for Vrx (1.23) + Egap (0.25) = Vtn (1.48)
cp = 527.  # J/(kg·K), at 300K, from http://www.surfacenet.de/html/barium_titanate.html

# further
m = 3.1 * 10**-3  # mass of pyro particles in kg
vrx = 1.23
vth = vrx + Egap  # in eV, H2O reaction energy thermo-neutral + band gap
```

```
# cube
acube = 80. * 10**-6  # cubic particle dimension of pyroelectric in m
a2cube = (acube)**2  # active surface area of pyroelectric in m^2
vcube = (acube)**3  # volume of pyroelectric cube in m^3
ncube = m/density/vcube
A = ncube*a2cube  # in m^2, only one of six faces is assumed active

eps0 = 8.8541878176 * 10**-12  #F m-1 (or A2 s4 kg-1 m-3 in SI base units)
F = 96485.3365  # C/mol

# calculation of obtained charge from temperature curve over time for specific pyroelectricum
T_c = 40. # in °C
T_h = 70. # in °C
heat = m * cp * (T_h - T_c)  # J

Eth = vth / acube  # electric field on pyroelectric as V/m
Eop = (vth - Egap) / acube

dt  = 0.1  # time step
t_cycle = 120.  # in seconds. Duration of one cycle: 2 min
times  = arange(0,t_cycle,dt)  # time array
T_t  = (T_h+T_c)/2.-(T_h-T_c)/2.*cos(2*pi*times/t_cycle)  # temperature over time
dTdt_t = 2*pi/t_cycle*(T_h-T_c)/2.*sin(2*pi*times/t_cycle)  # differential temperature over time

pyro_t = get_pyro(T_t,pyrocoeff)  # pyrocoeff. over time in µC/(m^2 K)

dQ_t = a2cube * pyro_t*10**-6 * dTdt_t * dt  # differential charge induced by pyroelectric
Qtot  = abs(dQ_t).sum() / 2.  # integrated absolute charge for one event

# voltage
epsilon_t = get_epsilon(T_t,epsilon)
dV_t  = acube * pyro_t*10**-6 * dTdt_t * dt / eps0 / epsilon_t  # threshold charge to build up
threshold voltage for chemical reaction
vvac = abs(dV_t).sum()/2.

# averages of p and epsilon
dp = pyro_t*10**-6 * dt
pav = dp.sum()/t_cycle
deps = epsilon_t * dt
epsav = deps.sum()/t_cycle

# graphical efficiency
Qth = 2. * vth * eps0 * epsav * acube  # derived from the capacitor equation. The factor 2
comes from the fact that two Qth produces a change in potential equal to 2vth
Qtot2 = vvac * eps0 * epsav * acube
Qrx = Qtot - Qth
Prx = Qrx / a2cube  # reaction-causing polarisation change in C/m^2

# Energy I
wtot = 2 * Qtot * vth  # work per particle
wpc = 2 * Qrx * vth  # J, total enclosed area - work obtained from the system per cycle
wd_PE = Prx * (Eth - Eop)  # J/m^3, as density
wrx = 2 * Qrx * vrx

# Efficiencies partial
```

```
etacarnot = 1. - ((T_c+273.15)/(T_h+273.15))
etath = Qrx / (Qrx + Qth)
etaop = vrx / vth
etaf  = 1
etachem = etath*etaop*etaf

# Efficiencies complete cycle
etapc = wpc * ncube / heat  # pyroelectric efficiency
etapc2 = 2 * Qtot * vth * etath * ncube / heat
etarx = etapc * etaop  # chequered areas = Qtot * 2. * vth * etath * etaop / heat
etanet = etarx * etaf

# Energy II per cycle
wrx2 = 2 * Qtot * vth * etath * etaop
wnet = wrx * etaf
wnet2 = 2 * Qtot * vth * etachem

# Hydrogen yield calculation
n = Qtot * ncube * 2. / 2. / F * etachem  # mol H2/cycle
V = n*24.465  # volume per cycle, 22.414 L/mol at 0 °C, 24.465 L/mol at 25 °C
ns = n/t_cycle  # mol H2/s
nd = ns*86400.  # mol H2/day
Vd = nd*24.465  # liter H2/day, 22.414 L/mol at 0 °C, 24.465 L/mol at 25 °C

DeltaH = 285900.  #  J/mol. Delta H of H2 + 0.5 O2 --> H2O
etacombust = n * DeltaH / heat

dpeT = pyro_t * 10**-6 / epsilon_t * dTdt_t * dt
DpeT = abs(dpeT).sum()/2  # /2 whenever we want the integral over one event.
dpeT2 = (pyro_t * 10**-6)**2 / epsilon_t * dTdt_t * dt
DpeT2 = abs(dpeT2).sum()/2

aopt = 4. * vth * eps0 / DpeT
acrit = 2. * vth * eps0 / DpeT
Tcrit = 2. * vth * eps0 / DpeT * (T_h - T_c) / acube
etanetmax = etaf * vrx / (8. * density * cp * vth * eps0) * DpeT2
fom = DpeT2 / eps0 / density / cp * etaop

hreport = 2. * n * 10**12 / m / 10**3 # in pmol/g.
```

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