Supplementary Materials for

Efficient Electrosynthesis of White Phosphorus from Molten Condensed Phosphate Salts

Jonathan F. Melville†, Andrew J. Licini†, Yogesh Surendranath*

Correspondence to: yogi@mit.edu

This PDF file includes:

Materials and Methods
Supplementary Text
Figs. S1 to S18
Tables S1 to S8
Contents

| Figure | Description | Page |
|--------|-------------|------|
| Figure S1 | Cutaway render of assembled high-temperature electrochemical reactor | 4 |
| Figure S2 | Exploded render of high-temperature reactor | 5 |
| Figure S3 | Diagram of molten-salt electrolysis setup | 6 |
| Figure S4 | Photos of graphite working-electrode morphologies | 8 |
| Figure S5 | Open-circuit potential trace of graphite pseudoreference electrode | 10 |
| Figure S6 | Simulated CVs for a putative EEC phosphate reduction mechanism | 14 |
| Figure S7 | Simulated CVs for a putative EECC phosphate reduction mechanism | 18 |
| Figure S8 | Photos of electrogenerated white and red phosphorus | 21 |
| Figure S9 | Photos of red phosphorus accretion on interior reactor surfaces | 22 |
| Figure S10 | $^{31}$P NMR spectrum of electrogenerated $P_4$ in CS$_2$ | 24 |
| Figure S11 | $^{31}$P NMR spectrum of dissolved polyphosphates from bleach trap | 25 |
| Figure S12 | Representative capacitive CVs for ECSA determination of graphite | 28 |
| Figure S13 | Representative linear fit for ECSA determination of graphite | 29 |
| Figure S14 | LSV traces of hollowed graphite electrode containing electrogenerated $P_4$ | 31 |
| Figure S15 | Photo of hollowed graphite electrode dosed with red phosphorus | 32 |
| Figure S16 | OCP traces of a various graphite electrode morphologies | 33 |
| Figure S17 | Classifications of condensed phosphate species | 36 |
| Figure S18 | Representative mechanism for oxide cleavage of phosphoryl anhydrides | 37 |

| Table | Description | Page |
|-------|-------------|------|
| Table S1 | Input parameters for simulated CVs by putative EEC mechanism | 12 |
| Table S2 | Simulation parameters for simulated CVs by putative EEC mechanism | 13 |
| Table S3 | Input parameters for simulated CVs by putative EECC mechanism | 16 |
| Table S4 | Simulation parameters for simulated CVs by putative EECC mechanism | 17 |
| Table S5 | Phosphate species and formulae by oxide and anhydride content | 38 |
| Table S6 | Selected condensed phosphate species investigated in this study | 40 |
| Table S7 | Molar heating input calculations for $P_4$ production process | 43 |
| Table S8 | Heat reclamation calculations for $P_4$ production process | 44 |
Materials and Methods

High-Temperature Electroanalytical Reactor Design

An electrochemical reactor (Figure 2, Figures S1-S3) was designed from the ground up to accommodate the electroanalysis of a molten-salt system while maintaining separation of cathodic and anodic gas flow streams. The main reactor body consisted of a closed-end alumina tube (designated “Alumina tube, one-end-closed, OD60.33mm*ID52mm*L279.4mm (OD+/-4%, ID+3/-0)” by AdValue Technologies), to which a custom-machined stainless-steel cap with four Swagelok™ Ultra-Torr® fittings could be attached. These fittings, as well as the junction between the reactor head and body, were sealed with DuPont™ Kalrez® perfluoroelastomer O-rings (temperature rated to 325 °C). Of the four fittings, three (of 1/4” diameter) held alumina-sheathed electrodes, while the fourth (of 3/4” diameter) held the isolated counter compartment and electrode. Careful management of the temperature of these O-rings, accomplished by glass insulation wool and Variac-controlled heating tape, is essential to reconcile the thermal rating of these O-rings with the temperatures of reaction; at low temperatures, P₄ will collect on the reactor head and interior instead of venting through the cold trap, while at high temperatures the O-rings will melt, eventually compromising the reactor seal. The furnace itself was designed to fit a CF56622C Lindberg/Blue M™ top-loading Crucible Furnace (now discontinued) as controlled by a CC58114C-1 Lindberg/Blue M™ Furnace Controller.
Figure S1. Cutaway render of assembled high-temperature electrochemical reactor.
Figure S2. Exploded render of high-temperature reactor, including component dimensions.
Figure S3. Diagram of molten-salt electrolysis setup configured for P₄ capture and quantitation, including separated cathodic and anodic N₂ gas flow streams.
Crucible Selection
The bottom of the electrochemical reactor contained a conical glassy carbon crucible (60 mL, 52 mm outer diameter (OD), part #39006KT from Alfa Aesar), so chosen for its inertness to the metaphosphate melt and the temperatures of reaction while under inert atmosphere. Between experiments, the crucible was polished with 800 grit sandpaper and an alumina slurry (1 micron deagglomerated hexagonal alumina powder, part #PSI-5601-5 by Precision Surfaces International, Inc.), then rinsed with reagent grade water (Millipore Type 1, 18.2 MΩ·cm resistivity). This polishing procedure was necessary to ensure that the fused melts could be easily separated from the crucible upon cooling following a reaction run.

Counter Compartment
For all experiments conducted in this study, the counter compartment consisted of a single-bore alumina tube (3/4" OD, 1/2" inner diameter (ID), 18" overall length, part #AL-T-N3/4-N1/2-18 by AdValue Technologies). Following the conclusion of these experiments, it was discovered that a clear fused quartz tube (19 mm OD, 15 mm ID, 1219 mm length, part #FQ-T-19-15-4 by AdValue Technologies, subsequently cut into 16"-long segments) was better suited to isolate the counter compartment. Quartz displayed enhanced resistance to corrosion in the presence of the molten metaphosphate electrolyte and its transparency allowed for visual inspection of the electrical contact made to the counter electrode.

Working Electrode
Unless indicated otherwise, the working electrode for all experiments was a graphite rod (Spectro-Grade: total impurity level < 2 ppm, individual element impurity levels < 1 ppm, 3/16” diameter, 12” length, part # 70231 by Electron Microscopy Sciences) with the end sharpened to a point in a pencil sharpener (Figure S4, center) and subsequently polished clean by rubbing with a Kimwipe™ to exfoliate potential trace metal impurities. In experiments which utilized a hollowed-electrode morphology, the end of a graphite rod (Spectro-Grade, 3/16” diameter, 12” length, part # 70231 by Electron Microscopy Sciences) was carved into a conical hollow using the corner of a razor blade (Figure S4, right), and subsequently polished clean by rubbing with a Kimwipe to exfoliate trace metal impurities. To prevent shorting of the electrode against the conductive reactor head, a single-bore alumina tube (1/4” OD, 3/16” ID, part #AL-T-N1/4-N3/16-12 by AdValue Technologies, cut to a length of approximately 4 inches) was used as an electrode sheath. Graphite electrodes were flame-sealed to the electrode sheath by using a propane blowtorch to melt a pea-sized volume of sodium metaphosphate salt, which was then dabbed onto the junction of the alumina sheath and the graphite electrode, adhering the two together.
Figure S4. Graphite working-electrode morphologies employed in the study: (a) an unaltered rod (b) a sharpened rod to facilitate release of electrogenerated gas bubbles, and (c) a rod modified with a concave depression to trap P₄ bubbles.
**Counter Electrode**

Unless indicated otherwise, the counter electrode for all experiments was a graphite rod (Spectro-Grade, 1/4” diameter, 12” length, part #70230 by Electron Microscopy Sciences™), the end polished by rubbing against a Kimwipe™ to exfoliate potential impurities. As this work focuses primarily on investigating the cathodic reduction of phosphate to elemental phosphorus, graphite was chosen as a sacrificial anode for these studies. The development of corrosion-resistant oxygen evolving anodes for high-temperature molten salt electrolysis is the subject of active ongoing investigations (50–54).

**Reference Electrodes**

All electrolytic experiments were performed using a graphite pseudoreference electrode. We found that this pseudoreference maintains a stable potential in a quiescent melt over long timescales, but the precise value of its potential was found to vary both within an experiment (due to local variations in melt composition induced by electrochemical action) and between experiments (due to alterations in the bulk composition of the melt). Thus, the graphite pseudoreference electrode was calibrated before and after each experiment against a liquid-sodium Na/Na⁺ absolute reference electrode (S4 Na/Al by Ionotec Ltd.). The solid-electrolyte junction of the sodium reference electrode was subject to slow corrosion in the metaphosphate electrolyte precluding its direct use as a full-time reference electrode. This calibration procedure minimized exposure of the Na/Na⁺ reference to the corrosive medium, but still allowed for comparison of the potentials across a variety of melt compositions. Further experimental details about the graphite pseudoreference and the Na/Na⁺ reference are provided below (33).
**Figure S5.** 5-minute open-circuit potential trace of graphite pseudoreference electrode against a Na/Na$^+$ reference electrode.
Graphite Pseudoreference

Unless indicated otherwise, the reference electrode for all experiments was a graphite rod (Spectro-Grade, 3/16” diameter, 12” length, part #70231 by Electron Microscopy Sciences™), the end polished clean by a Kimwipe™ to exfoliate potential impurities. To prevent shorting of the electrode against the conductive reactor head, a single-bore alumina tube (1/4” OD, 3/16” ID, part #AL-T-N1/4-N3/16-12 by AdValue Technologies, cut to a length of approximately 4 inches) was used as an electrode sheath. The graphite electrode was flame-sealed to the electrode sheath by using a propane blowtorch to melt a pea-sized volume of sodium metaphosphate salt, which was then dabbed onto the junction of the alumina sheath and the graphite electrode, adhering the two together.

Liquid Sodium Electrode

The liquid sodium reference electrode was custom-ordered from Ionotec Ltd. under the product designation “S4 Na/Al: Na beta-alumina reference electrode, 4.0 mm ID x 70 mm length x 0.6 mm wall thickness” and used as received.

Computational Modeling of Cyclic Voltammetry

To assess the plausibility of our putative mechanism and reconcile the activation-controlled current-overpotential relation in Figure 3 with the diffusion-controlled voltammograms seen in Figure 5, we employed Gamry™ Elchsoft™ DigiElch® Electrochemical Simulation Software to simulate hypothetical cyclic voltammetric behavior, as seen in Figure S6 and Figure S7. In an initial simulation, we modeled an EEC mechanism consisting of two consecutive fast electron-transfer steps followed by a comparatively slow chemical disproportionation. The first electron transfer (representing the reduction of $P_{V} \rightarrow P_{IV}$) occurred at an arbitrarily-selected potential of $E^\circ = 0 \text{ V}$ and a rapid $k_s = 1 \times 10^5 \text{ cm} \cdot \text{s}^{-1}$, while the second electron transfer (representing the reduction of $P_{IV} \rightarrow P_{III}$) was chosen to occur at $E^\circ = -0.1 \text{ V}$ with a slightly slower $k_s = 1 \times 10^4 \text{ cm} \cdot \text{s}^{-1}$; both reactions utilized a default symmetry factor of $\beta = 0.5$. The subsequent chemical reaction (representing the disproportionation of $P_{III} \rightarrow P_{(0)}$) was modeled with $k_f = 1 \times 10^{-4}$ and $K_{eq} = 1$. To represent the metaphosphate melt, the starting conditions for the simulation began at a concentration of 24 M for the simulated $P_{V}$ species, which possessed a rapid diffusion coefficient of 10 cm$^2$·s$^{-1}$. All other species began at a starting concentration of zero; the $P_{IV}$ and $P_{III}$ species were assigned a sluggish diffusion coefficient of $1 \times 10^{-20} \text{ cm}^2 \cdot \text{s}^{-1}$ to represent the likely surface-bound nature of these partially reduced intermediates, while the terminal $P_{(0)}$ species had a modestly faster diffusion coefficient of $1 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ to represent $P_4$ bubbling in the viscous electrolyte media.
Table S1. Input parameters for simulation of phosphate reduction to elemental phosphorus via a simulated EEC mechanism (Figure S6).

| Reaction       | Model              | $E^0$ (V) / $K_{eq}$ | ET Transfer Coefficient ($\alpha$) | $k_s$ (cm/s) / $k_f$ |
|----------------|--------------------|----------------------|------------------------------------|----------------------|
| $P^V + e^- \rightleftharpoons P^{IV}$ | Butler-Volmer      | 0                    | 0.5                               | $1 \times 10^5$      |
| $P^{IV} + e^- \rightleftharpoons P^{III}$ | Butler-Volmer      | $-0.1$               | 0.5                               | $1 \times 10^4$      |
| $P^{III} \rightleftharpoons P^{(0)}$      | Chemical Equilibrium | 1                    | N/A                               | $1 \times 10^{-5}$    |
Experimental Parameters:

|                |              |
|----------------|--------------|
| $E_{\text{start}}$ | 0.1 V       |
| $E_{\text{switch}}$ | $-0.2$ V    |
| $E_{\text{end}}$ | 0.1 V       |
| Scanrate(s)    | 100, 50, 25, 10 mV·s$^{-1}$ |
| Temperature    | 500 K        |
| $R_a$          | 1 $\Omega$  |
| $C_{\text{dl}}$ | $1\times10^{-5}$ F |
| Cycles         | 1            |

| Electrode geometry | Planar               |
|--------------------|----------------------|
| Area               | 1 cm$^2$             |
| Diffusion          | Semi-infinite 1D     |
| Pre-equilibrium    | All reactions        |

Species parameters:

|                 |              |
|-----------------|--------------|
| $[\text{P}^{\text{V}}]$ | 24 M         |
| $[\text{P}^{\text{IV}}]$ | 0 M          |
| $[\text{P}^{\text{III}}]$ | 0 M          |
| $[\text{P}^{(0)}]$    | 0 M          |

Table S2. Simulation parameters for simulation of phosphate reduction to elemental phosphorus via a simulated EEC mechanism (Figure S6).
Figure S6. Computationally modeled cyclic voltammograms, simulated by Gamry™ Elchsoft™ DigiElch® Electrochemical Simulation Software, for a putative EEC phosphate reduction mechanism consisting of two consecutive rapid electron-transfer steps followed by a comparatively slow chemical disproportionation. (a) displays the full CV simulation, while (b) displays a zoomed view of the simulated reductive feature.
We also performed additional simulations (Figure S7) on a putative EECC mechanism consisting of two consecutive electron-transfer steps $P^V \rightarrow P^{IV} \rightarrow P^{III}$, followed by a chemical disproportionation to a surface-bound phosphorus species (denoted “red P”) that proceeds towards a terminal white phosphorus product by a second chemical reaction. In this model, the partially reduced intermediates $P^{IV}$ and $P^{III}$ are not surface-bound; rather, the square-root scanrate dependence is evinced by the surface-bound nature of the intermediary chemically generated red P intermediate.
### Table S3. Input parameters for simulation of phosphate reduction to elemental phosphorus via a simulated EECC mechanism (Figure S7).

| Reaction                  | Model          | $E^0$ (V) / $K_{eq}$ | ET Transfer Coefficient ($\alpha$) | $k_s$ (cm/s) / $k_f$ |
|--------------------------|----------------|-----------------------|-----------------------------------|-----------------------|
| $P^{V} + e^- \rightleftharpoons P^{IV}$ | Butler-Volmer | 0                     | 0.5                               | $1 \times 10^5$      |
| $P^{IV} + e^- \rightleftharpoons P^{III}$ | Butler-Volmer | $-0.05$               | 0.5                               | $1 \times 10^4$      |
| $P^{III} \rightleftharpoons \text{red P}$ | Chemical Equilibrium | 1                     | N/A                               | 1                     |
| red P $\rightleftharpoons$ white P | Chemical Equilibrium | 1                     | N/A                               | 1                     |
**Experimental Parameters:**

| Parameter   | Value                  |
|-------------|------------------------|
| $E_{\text{start}}$ | 0.1 V                 |
| $E_{\text{switch}}$ | $-0.1$ V             |
| $E_{\text{end}}$   | 0.1 V                  |
| Scanrate(s)      | 100, 50, 25, 10 mV·s$^{-1}$ |
| Temperature      | 500 K                  |
| $R_u$            | 1 Ω                    |
| $C_{\text{dl}}$  | $1 \times 10^{-5}$ F  |
| Cycles          | 1                      |

| Electrode geometry | Planar |
|--------------------|--------|
| Area               | 1 cm$^2$ |
| Diffusion          | Semi-infinite 1D |
| Pre-equilibrium    | All reactions |

| Species parameters: | |
|---------------------|--|
| $[\text{P}^\text{V}]$ | 24 M $1 \times 10^{-5}$ cm$^3$·s$^{-1}$ |
| $[\text{P}^\text{IV}]$ | 0 M $1 \times 10^{-5}$ cm$^3$·s$^{-1}$ |
| $[\text{P}^{\text{III}}]$ | 0 M $1 \times 10^{-5}$ cm$^3$·s$^{-1}$ |
| red P              | 0 M $1 \times 10^{-20}$ cm$^2$·s$^{-1}$ |
| white P            | 0 M $10$ cm$^2$·s$^{-1}$ |

**Table S4.** Simulation parameters for simulation of phosphate reduction to elemental phosphorus via a simulated EECC mechanism (Figure S7).
Figure S7. Computationally modeled cyclic voltammograms, simulated by Gamry™ Elchsoft™ DigiElch® Electrochemical Simulation Software, for a putative EECC phosphate reduction mechanism consisting of two consecutive electron-transfer steps, followed by a chemical disproportionation to a surface-bound phosphorus species that proceeds towards a terminal phosphorus product by a second chemical reaction.
The simulated voltammograms seen in Figure S6 and Figure S7 reproduce the profile and scan-rate dependence of the diffusion-controlled voltammograms seen in Figure 3. In particular, the simulation captures the square-root scan-rate dependence of the reductive current densities as well as the presence of common potential corresponding to \( j=0 \) across all traces. **We stress that is qualitative similarity between simulated and experimental voltammograms should not be taken as an indication of the validity of the simulation parameters**; rather, these computations provide an explanation for the apparent contradiction between our observation of diffusion-controlled cyclic voltammograms (Figure 3) and the activation-controlled Tafel curves (Figure 5). In particular, the simulations indicate that an observed square-root scan-rate dependence in the CV may result not from diffusion limitation of a reactant species, but rather the build-up of reduced intermediates such as \( P^{(III)} \) and \( P^{(IV)} \) species in the reaction diffusion layer, a phenomenon which evinces itself if any electrochemically or chemically generated species following the initial phosphate reduction is bound to the electrode surface. This build-up may lead to a diffusion-limited back-oxidation current, which upon summing with a scan-rate independent reduction current, manifests as a diffusion-limited voltammogram. In particular, since \( j_{\text{tot}} = j_{\text{red}} - j_{\text{ox}} \), the lower \( j_{\text{tot}} \) observed at lower scan-rates is not due to reduced diffusion-limited \( j_{\text{red}} \), but increased diffusion-limited \( j_{\text{ox}} \). This phenomenon may be enabled by low gas solubility and product diffusion coefficients in the metaphosphate electrolyte, which means that slower scan rates have a greater buildup of reduced products near the electrode surface.

**Product Detection and Quantitation**

**Gas Flowthrough Setup**

In order to account for potential gas flow losses due to loss of O-ring seal integrity at temperature, a gas flowthrough setup (Figure S3) was constructed to enable quantitation of \( N_2 \) gas flow into and out of the electrochemical reactor, utilizing acrylic valved bead flowmeters (part #PB-3246040 by Cole-Parmer Scientific™) leading into and out of both the working and counter electrode compartments. Working compartment flowmeters were rated for between 40 to 500 standard cubic centimetres per minute (scm), while counter compartment flowmeters were rated for between 10 and 50 scm. At typical flowrates of 40 scm through the counter compartment and 400 scm through the working compartment, temperature effects due to volumetric expansion were found to be within the error of the system. In quantitating \( P_4 \) yield for calculating Faradaic efficiency (FE%), observed yield was normalized by working compartment gas outflow as a fraction of working compartment gas inflow. For analysis of counter electrode outflow streams, gas chromatography (GC) analysis was performed by injection into a Multi-Gas Analyzer (#3; SRI Instruments) equipped with a thermal conductivity detector, methanizer, and flame ionization detector in series after Molsieve 13x and Hayesep D Columns.

**Product Capture**

Evolved phosphorus was collected from three primary locations: the cold trap, the bleach trap, and the reactor head. The cold trap, immersed in a dry ice/acetone bath at -78 °C, was the primary method of capture and the only method by which molecular \( P_4 \) could be collected. To mitigate photoconversion of \( P_4 \) to polymeric red phosphorus (Figure S8), the bleach trap was wrapped in aluminum foil; following an experiment, the valves were sealed and the cold trap was pumped into a \( N_2 \) glovebox, within which \( P_4 \) samples for \( ^{31}P \) NMR could be prepared. The terminal bleach trap sometimes accumulated measurable quantities of phosphorus in the form of oxidized...
polyphosphate species, presumably formed by the oxidation of residual P$_4$ that exited the cold trap. Finally, polymeric red phosphorus deposits on the reactor interior (Figure S9), formed when the reactor head cooled below the 280.5 °C boiling point of P$_4$, were collected for quantification by oxidation and dissolution with bleach.
**Figure S8.** (a) Yellow-white crystals of white phosphorus are observed to form in the cold trap upon sustained electrolysis. (b) Upon exposure to light, electrogenerated white phosphorus will photoconvert to polymeric red phosphorus.
Figure S9. Post-electrolysis accumulation of red phosphorus on reactor body (a) and head (b) interiors.
**$^{31}$P NMR Analysis and Quantitation**

$^{31}$P NMR spectra were recorded with either Bruker AVANCE-400 or Bruker AVANCEDeo-500 spectrometers and processed using MestReNova software. $^{31}$P shifts are given in ppm with respect to externally referenced triphenylphosphine (TPP) ($\delta = -6.0$ ppm) or phosphonoacetic acid ($\delta = -17.0$ ppm). Coupling constants are reported as J-values in Hz.

**$^{31}$P NMR Identification of P₄**

For the collection of $^{31}$P NMR spectra of molecular P₄, such as that seen in Figure 3, the reactor cold trap (wrapped in aluminum foil) was sealed following a bulk electrolysis (typically around 50 mA·cm⁻² for several hours). The cold trap was then pumped into a N₂ glovebox, where the contents of the trap were dissolved with approximately 2 mL carbon disulfide (CS₂) along with a known quantity of triphenylphosphine (as an internal standard) as well as approximately 25 mg (0.072 mmol) of chromium(III) acetylacetonate as a paramagnetic relaxation agent. The sample was then transferred to a J. Young tube for $^{31}$P NMR analysis. To ensure full spin relaxation for quantitation, a delay time of 10.0 s was used.

**Quantitative $^{31}$P NMR**

Quantitative $^{31}$P NMR techniques were applied for the calculation of total reduced phosphorus yield. Phosphorus residues were collected from four primary locations: the cold trap, the bleach trap, surfaces within the reactor head, and the internal surfaces of the transfer lines. As we had already established the formation of P₄ with the preceding NMR in CS₂, for these experiments, we dissolve all products in a 7.4% w/w aqueous solution of sodium hypochlorite to facilitate the quantitation of all phosphorus emanating from the reactor. This bleach solution was used to oxidize elemental red phosphorus deposits (Figure S9) to soluble ortho- and polyphosphate species. These products were then quantified by aqueous $^{31}$P NMR against an internal standard of phosphonoacetic acid, again using a delay time of 10.0 s to ensure full spin relaxation for quantitation. For quantitation of phosphorus in the bleach trap, an aliquot was taken and analyzed against a phosphonoacetic acid internal standard to determine the concentration of phosphorus in the bleach trap, which was then multiplied by the volume of liquid in the bleach trap. The total phosphorus content in the bleach trap, cold trap, reactor head, and transfer lines were summed to determine the overall phosphorus yield, $N_P$. 
Figure S10. $^{31}P$ NMR spectrum of electrogenerated $P_4$ collected from cold trap, dissolved in CS$_2$ against a triphenylphosphine internal standard.
Figure S11. Representative quantitative $^{31}\text{P}$ NMR spectrum of bleach trap post-electrolysis. Integrals are normalized to phosphonoacetic acid internal standard at +17 ppm.
Calculation of Faradaic Efficiency

The Faradaic efficiency (FE%) of a process, also known as the current efficiency, is defined as the fraction of the total charge passed that proceeds towards a desired reaction product. We assess \( Q_{PRR} \) in coulombs for phosphate reduction from the total molar quantity of phosphorus \( N_P \) collected in the cold trap, bleach trap, reactor head, and transfer lines:

\[
Q_{PRR} = N_P \times \frac{5 \text{ mol e}^-}{1 \text{ mol P}} \times 96485 \text{ C.mol}^{-1}.
\]

We then normalize this observed value by the gas flow fraction \( m_{out}:m_{in} \) (as measured by the flow meters described above) to account for product losses from O-ring leakage, all of which occurs within the cell’s working compartment. Meanwhile, \( Q_{\text{total}} \) is determined from the current integral \( \int_0^t i_{total}(t) dt \), which for a galvanostatic experiment is merely \( i_{applied}t \). Putting these values together, we have:

\[
\text{FE\%} = \frac{N_P \times \frac{5 \text{ mol e}^-}{1 \text{ mol P}} \times 96485 \text{ C.mol}^{-1}}{i_{applied}t \times \frac{m_{out}}{m_{in}}},
\]

which for the NMR spectrum depicted in Figure S11 and its associated galvanostatic bulk electrolysis in Figure 3 gives us

\[
\text{FE\%} = \frac{1.40 \text{ mmol P} \times \frac{5 \text{ mol e}^-}{1 \text{ mol P}} \times 96485 \text{ C.mol}^{-1}}{75 \text{ mA} \times 13878 \text{ s} \times \frac{170 \text{ cm}^3\text{.min}^{-1}}{250 \text{ cm}^3\text{.min}^{-1}}}
\]

\[= 94.9\%.
\]

This value of 94.9% represents a peak observed value for flowthrough-normalized Faradaic efficiency. Preceding attempts at flowthrough-normalized FE% assessment recorded values of 51% (22.3% observed FE out of 45% gas flowthrough) and 76% (41.5% observed FE out of 55% gas flowthrough). We attribute this variability to the ingress of oxygen into the system due to O-ring seal failure at temperature, resulting in the pre-capture oxidation of evolved \( P_4 \). Next-generation molten-salt electrolysis reactors may seek to mitigate this factor by incorporating more temperature-resistant gaskets instead of the Kalrez O-rings used in this work.
Experimental Electrochemical Parameters

Unless specified otherwise, all electrochemical experiments were conducted with the furnace set to a temperature of 800 °C, which we found to correlate well to the internal equilibrated reactor temperature as measured by an internal thermocouple. Electrochemical data were collected using a Biologic VSP potentiostat using IR compensation values of no more than 20% for noncapacitive voltammetric studies, as higher values were found to induce IR overcompensation at modest current densities. Except where specified otherwise, a graphite electrode was employed as a pseudoreference electrode for all experiments, the potential of which was retroactively corrected for against a Na/Na+ reference that was briefly (15 seconds – 2 minutes) dipped into the melt before and after each experiment (see above). Uncompensated resistance (R_u) values were measured by the current-interrupt (CI) method; typical R_u values for the melt ranged from 1-10 Ω for all the electrolyte conditions, with higher-melting salts displaying greater solution resistances.

Calculation of Electrochemical Surface Area

Observed currents i were normalized to areal current densities j using electrochemical surface areas (ECSAs) assessed following adapted literature methodologies (55). For bare graphite electrodes, specific capacitance values in aqueous solution were found to be approximately 20 µF·cm⁻² relative to the geometric surface area, well in line with literature reports (56). Within the melt, specific capacitances of approximately 100 µF·cm⁻² for graphite were determined empirically from geometric surface area. Having determined these values, the ECSAs of an electrode could be determined in terms of the double-layer capacitances (DLCs) of the electrode, both in the melt preceding and following every experiment, as well as within the melt to assess the depth of electrode immersion and ensure the absence of a short between an electrode and the glassy carbon crucible. DLC values were assessed by CV scans spanning ±50 mV around the measured OCP, with three cycles each at scan rates of 10 mV·s⁻¹, 20 mV·s⁻¹, 30 mV·s⁻¹, 40 mV·s⁻¹ and 50 mV·s⁻¹ at IR compensations of 80%. The resultant capacitive CV traces (Figure S12) were used to calculate the total capacitive current i, as the difference of the cathodic current i_c and the anodic current i_a taken at the midpoints (OCP) of the capacitive curve. These currents are related to the overall electrode capacitance C by the relation

\[ C = \frac{1}{2} \frac{\partial (i_a - i_c)}{\partial \text{scanrate}} \]

Hence, the electrode capacitance (and hence ECSA) could be determined by plotting the capacitive currents as a function of scan rate and dividing the slope of the resulting linear fit, as demonstrated in Figure S13.
Figure S12. Representative cyclic voltammograms of a graphite electrode scanning ±50 mV around OCP at scanrates of 10 mV·s⁻¹, 20 mV·s⁻¹, 30 mV·s⁻¹, 40 mV·s⁻¹ and 50 mV·s⁻¹. Electrolyte is 0.1 M aqueous sodium perchlorate solution.
Figure S13. Representative linear fit for scan rate dependence of capacitive current at OCP in Figure S12. At an aqueous specific capacitance of 20 μF·cm⁻², this slope corresponds to an electrode surface area of 1.08 cm².
Collection of Cyclic Voltammetry Data

The collection of cyclic voltammetry data (Figures 3 and 5) entailed capacitive CV collection for ECSA determination followed by cyclic voltammetry scans beginning at the open-circuit potential and spanning ±350 mV around the solution OCP, with three scans each at scan rates of 10 mV·s⁻¹, 25 mV·s⁻¹, 50 mV·s⁻¹, and 100 mV·s⁻¹.

Current-Overpotential Studies

The collection of current-overpotential data for Tafel studies (Figure 5) entailed capacitive CV collection for ECSA determination, followed by chronopotentiometric steady state electrolysis. ECSA experiments were performed pre- and post-experiment in both aqueous and molten-salt conditions and found not to substantially differ; however, due to the fixed galvanostatic currents, variation in the electrode surface areas between experiments (due to variable depth of immersion in the melt) is responsible for the slight variation in areal current density values in these plots.

Collection of Galvanostatic Tafel Data

Electrolyses were performed galvanostatically with a fixed current series of 10 µA, 30 µA, 100 µA, 300 µA, 1 mA, 3 mA, 10 mA, 30 mA, 100 mA and 300 mA with 30 second traces and 30 second rest periods at open-circuit between electrolyses. Typically, chronopotentiometry traces reached steady state within 15 seconds. However, for traces in the transition region of the Tafel plots (Figure 5), the potential decayed to more negative values over the course of 30 seconds before reaching steady state. This slower approach to steady state is attributed to anhydride depletion local to the electrode. In all cases, the final potential at the conclusion of chronopotentiometry trace was taken as the steady-state value plotted in Figure 5. Each galvanostatic series was performed sequentially in triplicate in every experimental setup, and the experimental setups themselves were replicated between three and nine times each to account for random variations in reactor arrangement. Error bars were calculated from 95% confidence intervals as 1.95996 times the sample standard error.

Determination of Overpotential

Overpotentials for phosphate reduction were determined for each melt in this study relative to $E_{eq}$ values determined by the hollowed-electrode method. In particular, a hollowed electrode was immersed in each melt, and gently agitated to dislodge air bubbles trapped in the electrode hollow. $P_4$ was generated in the electrode hollow by reductive galvanostatic electrolysis at 10 mA·cm⁻² for one minute and then a 5-minute open-circuit trace was recorded (Figure S16). $E_{eq}$ was taken to be the minimum recorded OCP over this 5-minute trace, discounting double-layer relaxation immediately following electrolysis. This methodology was further vetted by post-galvanostatic anodic linear-sweep voltammetry (LSV) allowing a five-second post-electrolysis rest at OCP (Figure S14), as well as both analogous LSV and OCP studies on a red phosphorus-dosed hollow graphite electrode (Figure S15).
Figure S14. LSV traces of a hollowed graphite electrode following a 1-minute galvanostatic electrolysis at −10 mA·cm\(^{-2}\), scanning oxidatively from OCP at scan rates of 10 mV·s\(^{-1}\), 25 mV·s\(^{-1}\), 50 mV·s\(^{-1}\) and 100 mV·s\(^{-1}\).
**Figure S15.** A hollowed graphite working electrode, with the produced cavity smeared with red phosphorus for non-Faradaic *in situ* P₄ generation.
Figure S16. 5-minute OCP traces of a resting (pre-electrolysis) sharpened graphite electrode (green), sharpened (black) and hollowed (red) graphite electrodes following 1-minute galvanostatic electrolys at $-10 \text{ mA\cdotcm}^{-2}$, and a hollowed graphite electrode coated in red phosphorus (blue).
Methodology for Tafel Analysis

The relationship between the cathodic current density $j$ and the overpotential $\eta$ is defined by the Tafel equation:

$$\eta = -\frac{RT \ln 10}{\beta n F} \log_{10} \left[ \frac{j}{j_0} \right],$$

where $\beta$ is the symmetry factor for a single-step electrochemical reaction in which $n$ electrons are transferred and $j_0$ is the exchange-current density. The symmetry factor is defined as a number between 0 and 1, corresponding to the relative position of the activated complex as a fraction of the reaction coordinate from reduced to oxidized species. Experimentally determined symmetry factors typically range from 0.4 to 0.6, and hence $\beta$ is typically assumed to be 0.5 in nearly all cases (37). Meanwhile, the exchange-current density is defined as the equilibrium current density at net zero overpotential, at which the magnitudes of anodic and cathodic current are equal, thereby evincing no net electrolysis.

Generalizing the Tafel equation to a multistep case, we have

$$\eta = -\frac{RT \ln 10}{\alpha F} \log_{10} \left[ \frac{j}{j_0} \right],$$

in which the single-step symmetry factor-adapted electron transfer number $n\beta$ is replaced by the multi-step transfer coefficient

$$\alpha = \frac{\gamma}{\nu} + r\beta,$$

where $\gamma$ is the number of electrons transferred prior to the rate-limiting step (RLS), $\nu$ is the stoichiometric number of the reaction, $r$ is the number of electrons transferred in the RLS, and $\beta$ is the symmetry factor of the RLS (36–38). At 800 °C, this corresponds to a Tafel slope

$$b_{800 \, ^\circ C} = \frac{\partial \eta}{\partial (\log j)} = \frac{212.9 \, \text{mV} \cdot \text{dec}^{-1}}{\alpha}.$$

Tafel slopes and errors were assessed by least-squares linear fitting (using OriginLab Origin2018’s Linear Fit with Y Error algorithm to propagate errors) of the current-potential data in the ‘macropolarization’ regime, defined as current densities $\geq 1 \, \text{mA} \cdot \text{cm}^{-2}$. All Tafel slopes are reported in units of mV·dec$^{-1}$.

Gas Chromatography of Gas Outflow Streams

For analysis of counter electrode outflow streams, GC analysis was performed by injection of the effluent gas into a Multi-Gas Analyzer (#3; SRI Instruments) equipped with a thermal conductivity detector, methanizer, and flame ionization detector in series after Molsieve 13x and Haysep D Columns. With the counter compartment gas flowrate set to 60 sccm, baseline measurements were collected by injecting gas from the counter electrode outflow stream at rest, while experimental values were collected by injecting gas from the counter electrode outflow stream while passing a fixed cathodic current of 75 mA through the working electrode (and thereby an equivalent anodic current through the counter electrode).
The GC traces evince a significant increase in the gas fractions of CO and CO\(_2\) while the counter electrode is under anodic polarization relative to a control experiment without electrolysis. Integrating the GC traces reveals a gas outflow stream that is 96% CO\(_2\) and 4% CO, equivalent to a net electron efficiency of 3.9 electrons per atom of carbon, out of a theoretical 4 electrons per carbon for the total conversion of C \(\rightarrow\) CO\(_2\). This compares favorably to the value of 2 electrons per carbon for the incomplete combustion C \(\rightarrow\) CO used in the thermal process. The generation of CO may be attributable to either the partial oxidation of graphite and/or the Boudouard reaction, the comproportionation of CO\(_2\) with carbon, CO\(_2\) + C \(\rightleftharpoons\) 2 CO (57-59).

**Composition and Structure of Molten Condensed Phosphates**

Condensed phosphates are defined as phosphate salts that are dehydrated relative to free orthophosphate, possessing at least one phosphoryl anhydride linkage between adjacent phosphorus atoms. Collectively, the condensed phosphates comprise the linear polyphosphates, the cyclic metaphosphates, and the branched ultraphosphates (Figure S17). These phosphoryl anhydride linkages are crucial to describing the chemistry of the condensed phosphates, as their oxide-induced cleavage to terminal phosphates is fundamental to the ‘oxide-accepting’ character of condensed phosphate melts (Figure S18).

This reactivity allows condensed phosphate melts to intrinsically fulfill the role performed in the thermal process by the conversion of silicon dioxide to metasilicate, which is associated with a majority of the slag formation (and associated energetic losses) of the thermal process. Individual condensed phosphate species consist of a mixture of terminal, branching, and bridging moieties such that, by the relations detailed in Table S5, all condensed phosphate ions will satisfy the relation \([\text{PO}_{2.5\_u}\text{PO}_3\_m\text{PO}_{3.5\_p}]^{(m+2p)-}\), where \(u\) is the number of branching (ultraphosphate) moieties, \(m\) is the number of bridging (metaphosphate) moieties, and \(p\) is the number of terminal (paraphosphate) moieties. While the presence of fractional oxygen atoms for bridging and terminal phosphate groups may seem problematic at first, the nature of terminal and branching groups in a phosphate oligomer is such that the total number of bridging and terminal phosphates must always be an even number, so this is not an issue. For obvious reasons, free orthophosphate ions cannot be part of a condensed phosphate oligomer, as they have no phosphoryl anhydride linkages and hence are not condensed phosphates. The interconversion of phosphate oligomers – for example, of two paraphosphates into an orthophosphate and a metaphosphate, two metaphosphates into a paraphosphate and an ultraphosphate, or the reverse of these reactions – is expected to occur rapidly at the high temperature of the melt and, thus, we consider all molten phosphate species to be in equilibrium under the conditions of electrolysis (60). As the precise distribution of condensed phosphate chains is a function of temperature, precise characterization of a melt cannot be performed by analysis of the solidified electrolyte, although such post-solidification analysis vindicates our conflation of mixed orthophosphate-metaphosphate solutions with their equivalent pure polyphosphate melts (see below). Future studies on the *in situ* character of the melt (perhaps by high-temperature NMR) may permit quantification of the phosphate speciation in the reaction media.
Figure S17. Classifications of condensed phosphate species.
Figure S18. Representative mechanism for cleavage of a phosphoryl anhydride linkage by an oxide equivalent, here showing the formation of tripolyphosphate ($\text{P}_3\text{O}_{10}^{5-}$) from trimetaphosphate ($\text{P}_3\text{O}_9^{3-}$). Note that oxide equivalents rarely exist as free $\text{O}^{2-}$ ions, and in practice are more likely to be represented as nucleophilic polyphosphate chains.
| Prefix | Structure   | Anhydrides | Oxides | Formula Unit |
|--------|-------------|------------|--------|--------------|
| ortho- | free        | 0          | 1½     | PO₄³⁻        |
| para-  | terminal    | 1          | 1      | PO₃.₅²⁻      |
| meta-  | bridging    | 2          | ½      | PO₃         |
| ultra- | branching   | 3          | 0      | PO₂.₅      |

**Table S5.** Phosphate species by the number of phosphoryl anhydride linkages per phosphorus atom and their equivalent oxide content relative to phosphoric anhydride, P₄O₁₀.
Preparation of Selected Condensed Phosphate Mixtures

As seen in Table S6, four selected condensed phosphate melts of varying degrees of oxide content were selected for analysis in this work, spanning a range of phosphoryl anhydride molalities from 5.4 mol·kg\(^{-1}\) to 9.8 mol·kg\(^{-1}\). While the first of these melts was equivalent to a pure metaphosphate melt, the remainder were synthesized by mixing targeted mole fractions of sodium trimetaphosphate (S3MP) and sodium orthophosphate (SOP) to produce a homogenous electrolyte upon fusion. A 75:25 mol:mol mixture of S3MP:SOP (85:15 by mass) is 8.3 mol·kg\(^{-1}\) in phosphoryl anhydride linkages, equivalent to that of sodium decapolyphosphate (S10PP); a 50:50 mol:mol mixture (65:35 by mass) is 6.4 mol·kg\(^{-1}\), equivalent to sodium tetrapolyphosphate (S4PP); finally, a 40:60 mol:mol mixture (55:45 by mass) is 5.4 mol·kg\(^{-1}\), equivalent to sodium tripolyphosphate (S3PP). Lower concentrations of phosphoryl anhydride linkages are largely inaccessible as melts at the reaction temperature of 800 °C; the next lowest polyphosphate, sodium pyrophosphate (3.8 mol·kg\(^{-1}\) in phosphoryl anhydride linkages) has a melting point of 988 °C, and pure sodium orthophosphate (0 mol·kg\(^{-1}\) in phosphoryl anhydride linkages) has a melting point of 1583 °C. For each of these selected melts, a total mass of 60 g was measured out in the prescribed ratio of S3MP (99.9999%, anhydrous, #AA89063A1 from Alfa Aesar™) to SOP (99.9999%, anhydrous, #AC389810010 from Acros Organics™) and ground together in a mortar & pestle to ensure homogeneity. This mixture was then poured into a glassy carbon crucible for electroanalysis as described above.
| Melt Equivalent | [anhydride] | Na₃P₃O₉ mol% | Na₃PO₄ mol% |
|-----------------|-------------|--------------|-------------|
| S3MP (Na₃P₃O₉)  | 9.8076      | 100%         | 0%          |
| S10PP (Na₁₂P₁₀O₃₃) | 8.3210    | 75%          | 25%         |
| S4PP (Na₆P₄O₁₃) | 6.3883      | 50%          | 50%         |
| S3PP (Na₅P₃O₁₀) | 5.4368      | 40%          | 60%         |

**Table S6.** Condensed phosphate melts selected for study, their net anhydride content (in mol·kg⁻¹), their homogeneous equivalent species (in terms of melt oxide/anhydride content), and the molar ratios of sodium trimetaphosphate (S3MP) and sodium orthophosphate (SOP) required for synthesis.
Estimation of Power Efficiency

For Electrochemical Phosphate Reduction

Assuming 100% Faradaic efficiency for phosphate reduction at a fixed current of 0.300 A and an overall cell voltage of 1.00 V (a reasonable voltage estimate for an electrochemical system with a pure metaphosphate melt and a graphite anode, as observed in the voltammetric separation of cathodic and anodic processes in Figure 5 bottom):

\[
0.3 \text{ A} \times \frac{1 \text{ C}}{1 \text{ A}} \times \frac{1 \text{ mol e}^-}{96485 \text{ C}} \times \frac{1 \text{ mol P}_4}{20 \text{ mol e}^-} \times \frac{0.124 \text{ kg P}_4}{1 \text{ mol P}_4} \times 1 \text{ h} \times \frac{1 \text{ kW} \cdot \text{h}}{1000 \text{ W} \cdot \text{h}} \times 3600 \text{ s} \text{ h}^{-1}
\]

\[
= 3.00 \times 10^{-4} \text{ kW} \cdot \text{h} \text{ kg P}_4
\]

\[
= 4.32 \frac{\text{ kW} \cdot \text{h}}{\text{ kg P}_4}
\]

For Thermal Phosphoric Acid Dehydration

Because the proposed electrolysis process would remove phosphorus and oxygen ions from the melt while keeping the sodium ion content constant, the system will need to be replenished with a form of phosphorus oxide, i.e. phosphorus pentoxide (P\textsubscript{2}O\textsubscript{5}). While the actual process could input phosphoric acid directly with in-situ dehydration, the minimum work calculation is most easily performed by considering the following three stages:

1) \(2 \text{ H}_3\text{PO}_4 \rightarrow \text{P}_2\text{O}_5 + 3 \text{ H}_2\text{O}\) (dehydration of phosphoric acid to phosphorus pentoxide)
2) \(\text{P}_2\text{O}_5 + \text{Na}_3\text{PO}_4 \rightarrow \text{Na}_3(\text{PO}_3)_3\) (absorption of phosphorus pentoxide by orthophosphate equivalents in the melt, replenishing anhydride bonds)
3) \(2 \text{ Na}_3(\text{PO}_3)_3 + 5 \text{ C} \rightarrow \text{P}_4 + 2 \text{ Na}_3\text{PO}_4 + 5 \text{ CO}_2\) (electrolysis of metaphosphate)

Since metaphosphate is generated in step 2 and then immediately consumed in step 3, it is appropriate for the purposes of this analysis to treat orthophosphate-enriched metaphosphate as a temporary solvent for the reagent P\textsubscript{2}O\textsubscript{5} (analogously to cryolite acting as a solvent for electrolysis of Al\textsubscript{2}O\textsubscript{3} in the Hall-Héroult process). As a result, we can combine steps 2 and 3 as follows:

\[
2 \text{ P}_2\text{O}_5 + 5 \text{ C} \rightarrow \text{P}_4 + 5 \text{ CO}_2
\]

However, this reaction cannot be combined with step 1 without double-counting the electrical work, which we calculate experimentally in this paper, as part of the required enthalpy. As a result, the simplest thermodynamic cycle to calculate the additional heating costs would be as follows:
a) \(4 \text{H}_3\text{PO}_4 \rightarrow 2 \text{P}_2\text{O}_5 + 6 \text{H}_2\text{O} \), at room temperature.

b) \(2 \text{P}_2\text{O}_5 \) and \(6 \text{H}_2\text{O} \) are both heated and vaporized at the reaction temperature of 800 °C.

c) Following electrochemical reaction, the product gases \( \text{P}_4 \) and 5 \( \text{CO}_2 \), as well as the \(6 \text{H}_2\text{O} \) released from the phosphoric acid, are cooled to room temperature.

For simplicity, we will assume that all reactions and gas flows take place under 1 atm of pressure. Among these, only the first two steps and the heating of the stoichiometrically-consumed graphite electrode incur thermal costs, as calculated below:

| Reaction / Process | Calculations | Heat Input Requirements (per mol \( \text{P}_4 \)) |
|-------------------|--------------|--------------------------------------------------|
| \(4 \text{H}_3\text{PO}_4(l, \text{R.T.}) \rightarrow 2 \text{P}_2\text{O}_5(s, \text{R.T.}) + 6 \text{H}_2\text{O}(l, \text{R.T.})\) | \(\Delta H^\circ_{\text{f}}(\text{H}_3\text{PO}_4) = -1271.7 \text{kJ/mol} \) (61) \(\Delta H^\circ_{\text{f}}(\text{P}_2\text{O}_5) = -365.83 \text{kcal/mol} \times 4.184 \text{kJ/kcal} = -1530.63 \text{kJ/mol} \) (62) \(\Delta H^\circ_{\text{f}}(\text{H}_2\text{O}) = -285.82 \text{kJ/mol} \) (61) \(\Delta H^\circ_{\text{f}} = 2 \times (-1530.63 \text{kJ/mol}) + 6 \times (-285.82 \text{kJ/mol}) = -4 \times (-1271.7 \text{kJ/mol})\) | 310.6 kJ/mol |
| \(2 \text{P}_2\text{O}_5(s, \text{R.T.}) \rightarrow 2 \text{P}_2\text{O}_5(s, 633 \text{K})\) | Molar heat capacity of condensed \( \text{P}_2\text{O}_5 \) (i.e. 2 moles \( \text{P}_2\text{O}_5 \)) \(C_p \) \(= A + Br + C_tr + D_tr + E_tr (\text{J/mol})\) where \(t\) = temperature (K) / 1000 and \(A = 67.70925, B = 576.4548, C = -219.7520, D = 18.93072\) \(\text{kJ/mol}\) \(E = -0.774806\) (41) Integration of \(C_p\) from 298.15 K to 633.15 K | 95.3 kJ/mol |
| \(2 \text{P}_2\text{O}_5(s, 633 \text{K}) \rightarrow 2 \text{P}_2\text{O}_5(g, 633 \text{K})\) | \(\text{P}_2\text{O}_5\)'s low temperature form \(\Delta H^\circ_{\text{f}}\text{f,g,H}_2\text{O}(63)\) = \(22,800 \text{cal/mol} \) (63) Multiply by 4.184 \(\text{J/cal}\) and then by 2 for 2 moles | 191 kJ/mol |
| \(2 \text{P}_2\text{O}_5(g, 633 \text{K}) \rightarrow 2 \text{P}_2\text{O}_5(g, 1073 \text{K})\) | Molar heat capacity of gaseous \( \text{P}_2\text{O}_5 \) \(= A + Br + C_tr + D_tr + E_tr (\text{J/mol})\) where \(t\) = temperature (K) / 1000 and \(A = 318.4915, B = 1523.290, C = -3196.413, D = 2474.455\) and \(E = 3.855326\) \(\text{kJ/mol}\) (41) Integration of \(C_p\) from 633.15 K to 1073.15 K | 131 kJ/mol |
| \(6 \text{H}_2\text{O}(l, \text{R.T.}) \rightarrow 6 \text{H}_2\text{O}(l, 373 \text{K})\) | Molar heat capacity of liquid \( \text{H}_2\text{O} \) \(= A + Br + C_tr + D_tr + E_tr (\text{J/mol})\) where \(t\) = temperature (K) / 1000 and \(A = -203.6060, B = 1523.290, C = -3196.413, D = 2474.455\) and \(E = 3.855326\) \(\text{kJ/mol}\) (41) Integration of \(C_p\) from 298.15 K to 373.15 K, then 6 moles | 34.0 kJ/mol |
| \(6 \text{H}_2\text{O}(l, 373 \text{K}) \rightarrow 6 \text{H}_2\text{O}(g, 373 \text{K})\) | \(\Delta H^\circ_{\text{vap}}\) of water = 40.65 \(\text{kJ/mol}\) at 373 K (60), \(x_6 \) moles. | 244 kJ/mol |
| \(6 \text{H}_2\text{O}(g, 373 \text{K}) \rightarrow 6 \text{H}_2\text{O}(g, 1073 \text{K})\) | Molar heat capacity of gaseous \( \text{H}_2\text{O} \) \(= A + Br + C_tr + D_tr + E_tr (\text{J/mol})\) where \(t\) = temperature (K) / 1000 and \(A = 30.09200, B = 6.832514, C = 6.793435, D = -2.534480\) and \(E = 0.082139\) \(\text{kJ/mol}\) (41) Integration of \(C_p\) from 373.15 K to 1073.15 K, then \(x_6 \) moles. | 159 kJ/mol |
| \(5 \text{C}(s, \text{R.T.}) \rightarrow 5 \text{C}(s, 1073 \text{K})\) | Heat capacity of graphite by mass (cal g\(^{-1}\) K\(^{-1}\)) \(= C_p = 6.603075 \times 1.60535 \times 10^{-4} T - 225.861 T^2 + 3100.10 T^3 - 910737.0 T^4 - 9.64607 \times 10^{-7} T^5\) (64) Integration from 298 to 1073 K yields 192 cal/g, then convert to \(\text{kJ}\) and multiply by 5 moles C | 48.3 kJ/mol |

**Total reaction / reactant heating inputs**

Partial Totals: 310.6 kJ/mol (dehydration reaction) + 417 kJ/mol (heating of \( \text{P}_2\text{O}_5 \) and phase transitions) + 437 kJ/mol (heating of \( \text{H}_2\text{O} \) and phase transitions) + 48.3 kJ/mol (heating of C) = 1,210 kJ/mol, or 2.7 kWh/kg \( \text{P}_4 \)
Table S7. Estimated molar heating input calculations for a putative P₄ production process, assuming pure liquid H₃PO₄ and no heat of mixing.

Practically speaking, phosphoric acid produced by the industrial wet process is only 26-30% P₂O₅:H₂O by weight (65) which, when the average of 28 wt% is converted into a molar ratio, is roughly 4.7 mol% or 1 mole of P₂O₅ per 20.3 moles of water. This would add an extra 20.3 moles to the water being heated per mole of P₂O₅, for a rough total of 46.6 total units of water per unit of P₄ (including waters of dehydration) – so the existing water heating costs must be adjusted by a scaling factor of (46.6 mol / 6 mol) × 437 kJ/mol = 3390 kJ/mol. Relatively to the calculation in Table S7, this introduces an additional water heating requirement of 2,950 kJ/mol.

This introduces another consideration; as a non-ideal mixture, the dissolution of pure phosphoric acid into water will be exothermic – meaning that in this theoretical thermodynamic cycle, additional heat will be needed to concentrate the industrial-grade phosphoric acid (with a weight percent of ~28 wt% P₂O₅ and thus ~63 wt% of H₃PO₄) into the pure liquid used in the thermochemical reaction calculation. The relative apparent molal heat content \( \phi_L \) of H₃PO₄ (which corresponds to the enthalpy released by dissolving H₃PO₄ of a given concentration into water until infinite dilution is reached), has been determined experimentally to follow the equation

\[
\phi_L = 292.06 + 923.79w + 3374.87w^2 - 2478.92w^3 + 3473.99w^4
\]

where \( w \) = the weight fraction (66). This formula yields values of 5600 cal/mol and 2100 cal/mol when \( w = 1 \) and 0.63, respectively, and, therefore, the theoretical heat energy required to reverse the exothermic dilution from pure H₃PO₄ to the industrial 63 wt% H₃PO₄ is 3400 cal/mol or 14 kJ/mol. Because four moles of phosphoric acid are required per mole of P₄, this raises the total heating costs by an additional 58 kJ/mol P₄.

Adjusting for the additional water heating costs in the final total of Table S7 and adding the heat energy lost from working against the exothermic dissolution of H₃PO₄ into water results in a newly adjusted heat energy total, when starting from industrial-grade wet process phosphoric acid, of 4220 kJ/mol or 9.4 kWh/kg P₄.

Given the electrical costs of our electrolysis are calculated to be ~4.3 kWh/kg, this worst-case-scenario total of 13.7 kWh/kg corresponding to no thermal recovery already falls comfortably within the 12.5-14 kWh/kg requirements of the industrial thermal process (7) while cutting the CO₂ emissions in half. However, much of the thermal energy input to heat the reagents can be reclaimed via heat exchange with the cooling product gases (P₄ and CO₂) as well as the steam released in the dehydration process.
The theoretical heat released by cooling the steam back to room temperature should be the same as the cost of its original heating, i.e. 3390 kJ/mol. However, we must also calculate the heat that would be released by the P4 and CO2 as they cool to 75 °C / 348 K (a reasonable storage temperature for P4 at which it is liquid) and room temperature, respectively (Table S8). (The cooling of the products theoretically releases slightly more thermal energy than the heating of the reagents requires, but this is thermodynamically expected because the electrolysis which separates the two steps involves a large external input of energy.)

| Reaction / Process | Calculations | Heat Recovery (per mole P4) |
|--------------------|--------------|-----------------------------|
| 46.6 H2O(l, 1073 K) → 46.6 H2O(l, R.T.) | -437 kJ/mol (from H2PO4(aq)) + 2953 kJ/mol (additional H2O of dilution) | -3,390 kJ/mol |
| P4(g, 1073 K) → P4(g, 553 K) | Molar heat capacity of gaseous P4 = C_p = A + Br + Ct + Dt + Et (J/mol) where t = temperature (K) / 1000 and A = 81.38466, B = 1.499484, C = -0.405575, D = 0.034585 and E = -1.327329. (41) Integration of C_p from 1,073.15 K to 553.15 K. | -44.5 kJ/mol |
| P4(g, 553 K) → P4(l, 553 K) | The ΔH_op of P4 is 545 J/g at 560 K (67), which will be close to that at 553 K. | -67.5 kJ/mol |
| P4(l, 553 K) → P4(l, 348 K) | Molar heat capacity of molten P = C_p = A + Br + Ct + Dt + Et (J/mol) where t = temperature (K) / 1000 and A = 26.3260, B = 1.041373×10^-10, C = -6.121360×10^-11, D = 1.094033×10^-11 and E = 2.995196×10^-12. (41) Essentially constant C_p, so heat released = (26.3260 J/mol mK) ((348 − 553 K) / 1000), then x4 moles. | -21.6 kJ/mol |
| CO2(g, 1073 K) → CO2(g, R.T.) | Molar heat capacity of gaseous CO2 = C_p = A + Br + Ct + Dt + Et (J/mol) where t = temperature (K) / 1000 and A = 24.99735, B = 55.18696, C = -33.69137, D = 7.948387 and E = -0.136638. (41) Integration of C_p from 1,073.15 K to 298.15 K, then x5 moles. | -935 kJ/mol |
| Total product cooling gains (assuming 100% efficiency) | Partial Totals: -3390 kJ/mol (cooling of H2O and phase transitions) - 133.6 kJ/mol (cooling of P4 and phase transitions) - 935 kJ/mol (cooling of CO2) | -4,460 kJ/mol |

Table S8. Calculation of total reclaimable heat energy of the products for an H3PO4-fueled P4 production cell.

However, not all of this heat energy can be directly reclaimed at 100% efficiency. In order to calculate the true efficiency of heat energy transfer for a counterflow heat exchanger for this process, one must calculate R, the ratio of the product of molar heat capacity and molar flow rate for the hot and cold streams. (68) This value is different for each input and output stream, and is further complicated by the presence of phase transitions which cause the R value to vary along different regions of the exchange contact area. However, even as R changes from its minimum of 0 to its maximum of 1, the efficiency of thermal transfer only varies from 100% to 85% at its asymptote. Since a detailed plant design is beyond the scope of this research, we will (for simplicity) conservatively assume a blanket thermal energy transfer efficiency of 80% for all chemical streams; this value assumes the worst possible transfer efficiency from R = 1 in conjunction with minor losses due to thermal leaks.
Based on this, we take 4220 kJ/mol heating total derived above and deduct 80% of the theoretical heat energy of the products (Table S8) of 4460 kJ/mol to arrive at total system heat input estimate of 652 kJ/mol = 1.5 kWh/kg P₄:

By these methods, we estimate that the combined energy costs incurred by electrolysis and heating total to ~5.8 kWh/kg, which is ~46% of the total energy costs of the modern industrial thermal process.