A New Concept for Producing White Phosphorus: Electrolysis of Dissolved Phosphate in Molten Chloride

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ABSTRACT: Producing white phosphorus exclusively by carbothermic reduction of phosphate rock is extremely energy-intensive and environmentally unfriendly. As for now, the phosphorus-making industry worldwide is thus disappearing, while the market demand for white phosphorus, spurred by fine chemicals and high-tech devices, is increasing. Technical defects have posed challenges to the downstream sectors relying on phosphorus-derived chemicals. This work presents a new concept for producing white phosphorus by electrolysis. Phosphate dissolved in a solvent can be electrochemically converted to elemental phosphorus. The concept was demonstrated by conducting experiments in the molten salt system of $CaCl_2$-$Ca_3(PO_4)_2$. $Ca_3(PO_4)_2$ dissolves in molten $CaCl_2$ to form a solution containing diffusible and electrochemically reducible phosphate ions. Electrolyzing the molten bath of $CaCl_2$-$Ca_3(PO_4)_2$ (2 mass %) at a constant potential of −2.48 V (vs Cl_2/Cl^-) at 850 °C results in continuous evolution of gaseous phosphorus on the cathode. Producing white phosphorus by electrolysis shows substantial advantages over the conventional carbothermic reduction technology in simplicity, energy efficiency, and cleanness. This work may lead to an upgrading of the phosphorus-making industry toward a cleaner and more sustainable production.

KEYWORDS: *Phosphorus, Clean production, Calcium phosphate, Calcium chloride, Electrolysis*
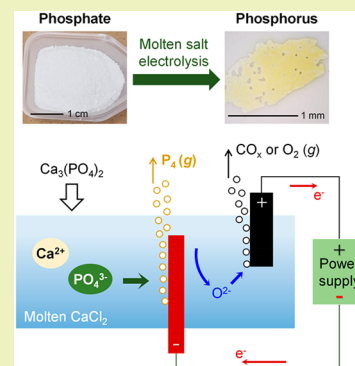
INTRODUCTION

White phosphorus (P_4) is the starting material for various critical chemicals, such as phosphoric acids, chlorides, sulfides, and phosphides.[1] The global demand for white phosphorus is increasing in recent years. However, the phosphorus-making industry is fast vanishing because the production process is highly energy intensive and environmentally unfriendly. Currently, production of white phosphorus is limited in countries (China, Kazakhstan, Vietnam, and the United States) with low electricity price or loose environmental regulations. The supply of white phosphorus is remarkably influenced by the national trade policies.[2] As a result, despite its importance, white phosphorus is becoming more and more difficult to obtain in the market. Addressing the challenges of securing a stable supply of white phosphorus is urgent for most industrial countries.

White phosphorus is produced by heating a mixture of phosphate rock [$Ca_3(PO_4)_2$], sand (SiO_2), and coke (C) in an electric furnace to a temperature about 1500 °C.[3−5] This process was invented in 1889[4,6] and has failed to keep the pace with the times. The process consumes a huge amount of energy [14−18 MWh per ton of phosphorus[7,8]] because reduction of $Ca_3(PO_4)_2$ by carbon is strongly endothermic. Quality control is difficult because of easy contamination by impurity elements at such a high temperature. Further purification is required to produce a high purity product. Moreover, emission of hazardous byproducts causes serious environmental problems. Technological innovations to achieve a cost-effective and clean production is urgently needed for the last surviving phosphorus-making plants and their customers.

Extraction of phosphorus by electrochemical techniques may be an alternative to carbothermic reduction due to the advantages in simplicity and cleanness. Several attempts in history can be found.[9−12] Metaphosphates with low melting points were once utilized as the electrolyte. Gruber[9] filed a patent in 1957 to produce phosphorus by electrolyzing molten $NaPO_3$. Caton et al.[10] in 1963 successfully obtained phosphorus by electrolyzing molten $NaPO_3$ or $LiPO_3$-KPO_3. However, these studies did not result in a practical production. Metaphosphates are not suitable to perform the role as an electrolyte due to the large viscosity.[10,13] Laitinen et al.[11] in 1966 and Franks et al.[12] in 1970 studied the electroreduction behavior of sodium phosphates in molten LiCl-KCl or NaCl-KCl. However, no proof of phosphorus formation was given in their paper, perhaps due to the poor diffusion of phosphate in the above-mentioned chlorides. Further research on this subject could be rarely found in the literature after the 1970s.
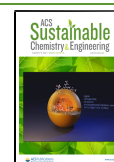
This paper proposes a new concept for producing white phosphorus: electrolysis of dissolved phosphate in molten salt. The concept was demonstrated by conducting experiments in the molten salt system of $CaCl_2$-$Ca_3(PO_4)_2$. $Ca_3(PO_4)_2$ is the phosphorus precursor, and molten $CaCl_2$ is the solvent. Since $CaCl_2$ is an excellent high temperature electrolyte widely used for materials synthesis[14−19] and $Ca_3(PO_4)_2$ is soluble in molten $CaCl_2$,[20] continuous formation of white phosphorus in a gas form is realized by electrolyzing the molten bath of $CaCl_2$-$Ca_3(PO_4)_2$. This finding may lead to an upgrading of the phosphorus-manufacturing industry toward a cleaner and more sustainable production.

■ THERMODYNAMIC ANALYSIS

Although $Ca_3(PO_4)_2$ has a rather high melting point (1670 °C), it is soluble in molten $CaCl_2$. According to the phase diagram reported by Epperlein,[20] solubility of $Ca_3(PO_4)_2$ in $CaCl_2$ is approximately 3 mass % at 800 °C and 11 mass % at 1000 °C. This feature leads us to the hypothesis that phosphorus could be produced by electrolyzing the molten bath of $CaCl_2$-$Ca_3(PO_4)_2$.
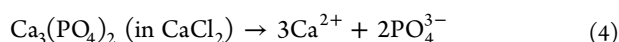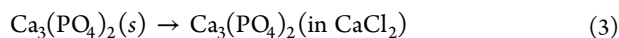
It is believed that 850 °C will be an optimum temperature to utilize the molten bath of $CaCl_2$-$Ca_3(PO_4)_2$, considering the solubility of $Ca_3(PO_4)_2$ and the vapor pressure of molten $CaCl_2$. In order to investigate the thermodynamics of redox reactions in molten $CaCl_2$−$Ca_3(PO_4)_2$, the chlorine evolution reaction on a hypothetical inert anode is taken as the reference

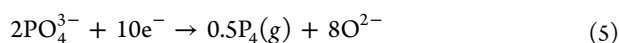$$2Cl^- \rightarrow Cl_2(g) + 2e^- \quad (1)$$

$$E_{Cl_2/Cl^-} = E^0_{Cl_2/Cl^-} + \frac{RT}{2F} \ln \frac{p_{Cl_2}}{a^2_{Cl^-}} \quad (2)$$

where E_{Cl_2/Cl^-} and $E^0_{Cl_2/Cl^-}$ are the nonstandard and standard chlorine evolution potentials in the molten bath, respectively; R is the gas constant ($R = 8.314$); T is temperature (Unit: K); F is the Faraday constant ($F = 96485$ C mol^{-1}); p_{Cl_2} is the partial pressure of Cl_2 (g); a_{Cl^-} is the activity of Cl^- ions, relative to pure $CaCl_2$. Here, the partial pressure of Cl_2 (g) is taken as 1 atm. Since only a limited amount of $Ca_3(PO_4)_2$ is dissolved, the activity of $CaCl_2$, a_{CaCl_2}, is approximated as unity. Activity of Ca^{2+} and Cl^- ions, $a_{Ca^{2+}}$ and a_{Cl^-}, is also taken as unity ($a_{CaCl_2} = a_{Ca^{2+}}$ $a^2_{Cl^-} = 1$; $a_{Ca^{2+}} = 1$; $a_{Cl^-} = 1$). Therefore, the chlorine evolution potential is considered to be constant ($E_{Cl_2/Cl^-} = E^0_{Cl_2/Cl^-}$).

Solid $Ca_3(PO_4)_2$ would dissolve and dissociate in molten $CaCl_2$ by

$$Ca_3(PO_4)_2(s) \rightarrow Ca_3(PO_4)_2 (\text{in } CaCl_2) \quad (3)$$

$$Ca_3(PO_4)_2 (\text{in } CaCl_2) \rightarrow 3Ca^{2+} + 2PO_4^{3-} \quad (4)$$

It is hypothesized that elemental phosphorus (P_4) can be extracted from phosphate ions in the molten bath by electrochemical deoxidation

$$2PO_4^{3-} + 10e^- \rightarrow 0.5P_4(g) + 8O^{2-} \quad (5)$$

$$E_{PO_4^{3-}/P_4} = E^0_{PO_4^{3-}/P_4} + \frac{RT}{10F} \ln \frac{a^8_{O^{2-}}}{p^0_{P_4} a^2_{PO_4^{3-}}}$$
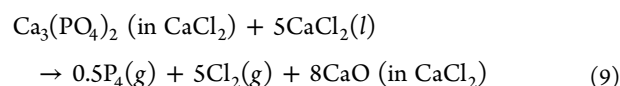$$= E^0_{PO_4^{3-}/P_4} + \frac{RT}{10F} \ln \frac{a^8_{O^{2-}}}{a^2_{PO_4^{3-}}} \quad (6)$$

where $E_{PO_4^{3-}/P_4}$ and $E^0_{PO_4^{3-}/P_4}$ are the nonstandard and standard occurring potentials of phosphorus extraction in the molten bath, respectively; p_{P_4} is the partial pressure of P_4 (g); $a_{O^{2-}}$ and $a_{PO_4^{3-}}$ are the activities of O^{2-} and PO_4^{3-} ions [relative to pure CaO and $Ca_3(PO_4)_2$], respectively. Here, the partial pressure of P_4 (g) is taken as 1 atm. The total reaction of phosphorus extraction coupled with chlorine evolution can be obtained by combining reactions 1 and 5

$$2PO_4^{3-} + 10Cl^- \rightarrow 0.5P_4(g) + 5Cl_2(g) + 8O^{2-} \quad (7)$$
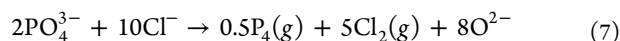
The phosphorus extraction potential with reference to chlorine evolution potential is

$$E_{PO_4^{3-}/P_4} - E_{Cl_2/Cl^-} = E^0_{PO_4^{3-}/P_4} - E^0_{Cl_2/Cl^-} - \frac{RT}{10F} \ln \frac{a^8_{O^{2-}}}{a^2_{PO_4^{3-}}} \quad (8)$$

Considering the standard state of each ion, reaction 7 and eq 8 can also be written as

$$Ca_3(PO_4)_2 (\text{in } CaCl_2) + 5CaCl_2(l)$$
$$\rightarrow 0.5P_4(g) + 5Cl_2(g) + 8CaO (\text{in } CaCl_2) \quad (9)$$

$$E_{PO_4^{3-}/P_4} - E_{Cl_2/Cl^-}$$
$$= E^0_{PO_4^{3-}/P_4} - E^0_{Cl_2/Cl^-} - \frac{RT}{10F} \ln \frac{a^8_{CaO}}{a_{Ca_3(PO_4)_2}} \quad (10)$$

where a_{CaO} and $a_{Ca_3(PO_4)_2}$ are the activities of dissolved CaO and $Ca_3(PO_4)_2$ relative to their pure solid state, respectively. The phosphorus extraction potential (vs Cl_2/Cl^-) at standard state can be calculated by

$$E^0_{PO_4^{3-}/P_4} - E^0_{Cl_2/Cl^-} = -\frac{\Delta_r G^0_{(9)}}{10F} \quad (11)$$

$$\Delta_r G^0_{(9)} = 8\Delta_f G^0_{CaO} - 5\Delta_f G^0_{CaCl_2} - \Delta_f G^0_{Ca_3(PO_4)_2} \quad (12)$$

where $\Delta_r G^0_{(N)}$ is the standard Gibbs energy change of reaction (N); $\Delta_f G^0_i$ is the standard Gibbs energy of formation of compound i. By using the thermochemical data listed in Table 1,

Table 1. Standard Gibbs Energy of Formation ($\Delta_f G^0$) of Some Compounds at 850 °C

species	state	$\Delta_f G^0$/kJ mol^{-1}	refs
$Ca_3(PO_4)_2$	s	−3211.3	21
CaO	s	−518.2	21
$CaCl_2$	l	−629.2	21
Ca_3P_2	s	−462.9	22
CO	g	−211.1	21
CO_2	g	−396.0	21

$\Delta_r G^0_{(9)}$ and $E^0_{PO_4^{3-}/P_4} - E^0_{Cl_2/Cl^-}$ at 850 °C are calculated to be 2211.7 kJ mol^{-1} and −2.29 V, respectively. Therefore, the phosphorus extraction potential (vs Cl_2/Cl^-) at the non-standard state at 850 °C is

$$E_{PO_4^{3-}/P_4} - E_{Cl_2/Cl^-}$$
$$= -2.29 - 0.178\log a_{CaO} + 0.022\log a_{Ca_3(PO_4)_2} \quad (13)$$

Table 2. Possible Half-Cell Redox Reactions in the Molten Bath of $CaCl_2$-$Ca_3(PO_4)_2$ and Their Occurring Potentials with Reference to Chlorine Evolution Potential at 850 °C

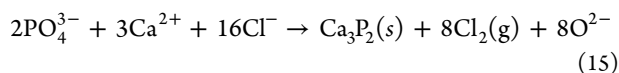| half-cell redox reaction	occurring potential/V vs Cl_2/Cl^-	
	standard	nonstandard
$2PO_4^{3-} + 10e^- \rightarrow 0.5P_4(g) + 8O^{2-}$	−2.29	$-2.29 - 0.178 \log a_{CaO} + 0.022 \log a_{Ca_3(PO_4)_2}$
$2PO_4^{3-} + 3Ca^{2+} + 16e^- \rightarrow Ca_3P_2(s) + 8O^{2-}$	−2.36	$-2.36 - 0.111 \log a_{CaO} + 0.014 \log a_{Ca_3(PO_4)_2}$
$O_2(g) + 4e^- \rightarrow 2O^{2-}$	−0.58	$-0.58 - 0.111 \log a_{CaO}$
$CO(g) + 2e^- \rightarrow C(s) + O^{2-}$	−1.67	$-1.67 - 0.111 \log a_{CaO}$
$CO_2(g) + 4e^- \rightarrow C(s) + 2O^{2-}$	−1.60	$-1.60 - 0.111 \log a_{CaO}$
$Ca^{2+} + 2e^- \rightarrow Ca(l)$		−3.26
$Cl_2(g) + 2e^- \rightarrow 2Cl^-$		0

[a]All redox reactions are written in the form of $Ox + ne^- \rightarrow Red$. [b]Activities of species other than CaO (or O^{2-}) and $Ca_3(PO_4)_2$ (or PO_4^{2-}) are taken as unity. [c]$a_{CaO} = a_{O^{2-}}$, $a_{Ca_3(PO_4)_2} = a_{PO_4^{3-}}^2$.

Since phosphorus may react with calcium to form Ca_3P_2 (s), the electrochemical formation of Ca_3P_2 (s) in the molten bath is also considered

$$2PO_4^{3-} + 3Ca^{2+} + 16e^- \rightarrow Ca_3P_2(s) + 8O^{2-} \quad (14)$$
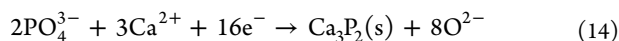
The total reaction of Ca_3P_2 (s) formation coupled with chlorine evolution can be obtained by combining reactions 1 and 14.

$$2PO_4^{3-} + 3Ca^{2+} + 16Cl^- \rightarrow Ca_3P_2(s) + 8Cl_2(g) + 8O^{2-} \quad (15)$$

Reaction 15 can also be written as

$$Ca_3(PO_4)_2 \text{ (in } CaCl_2) + 8CaCl_2(l)$$
$$\rightarrow Ca_3P_2(s) + 8Cl_2(g) + 8CaO(\text{in } CaCl_2) \quad (16)$$
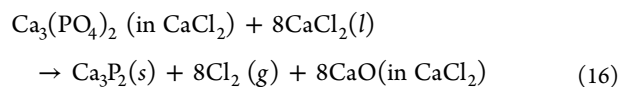
The formation potential of Ca_3P_2 (s) with reference to chlorine evolution potential is

$$E_{PO_4^{3-}/Ca_3P_2} - E_{Cl_2/Cl^-}$$
$$= E_{PO_4^{3-}/Ca_3P_2}^0 - E_{Cl_2/Cl^-}^0 - \frac{RT}{16F} \ln \frac{a_{CaO}^8}{a_{Ca_3(PO_4)_2}} \quad (17)$$

$$E_{PO_4^{3-}/Ca_3P_2}^0 - E_{Cl_2/Cl^-}^0 = -\frac{\Delta_r G_{(16)}^0}{16F} \quad (18)$$

$$\Delta_r G_{(16)}^0 = 8\Delta_f G_{CaO}^0 + \Delta_f G_{CaCl_2}^0 - 8\Delta_f G_{CaCl_2}^0 - \Delta_f G_{Ca_3(PO_4)_2}^0 \quad (19)$$

Ca_3P_2 (s) is considered to be insoluble in the molten bath and the activity of which is taken as unity. $\Delta_r G_{(16)}^0$ and $E_{PO_4^{3-}/Ca_3P_2}^0 - E_{Cl_2/Cl^-}^0$ at 850 °C are calculated to be 3636.4 kJ mol^{-1} and −2.36 V, respectively. Therefore, the formation potential of Ca_3P_2 (s) (vs Cl_2/Cl^-) at nonstandard state at 850 °C can be obtained

$$E_{PO_4^{3-}/Ca_3P_2} - E_{Cl_2/Cl^-}$$
$$= -2.36 - 0.111 \log a_{CaO} + 0.014 \log a_{Ca_3(PO_4)_2} \quad (20)$$

Other possible half-cell redox reactions in the system include

$$Ca^{2+} + 2e^- \rightarrow 2Ca(l) \quad (21)$$

$$2O^{2-} \rightarrow O_2(g) + 4e^- \quad (22)$$

If using carbon electrode, the following reactions may also occur

$$C(s) + O^{2-} \rightarrow CO(g) + 2e^- \quad (23)$$

$$C(s) + 2O^{2-} \rightarrow CO_2(g) + 4e^- \quad (24)$$
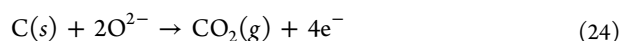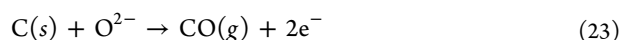
The occurring potentials of these reactions can be calculated in the same way as mentioned above. Table 2 summarizes the possible half-cell redox reactions in the molten bath of $CaCl_2$-$Ca_3(PO_4)_2$ and their occurring potentials with reference to chlorine evolution potential at 850 °C.

Figure 1 plots the potential-log a_{CaO} diagram for the reactions listed in Table 2. Increasing the CaO activity leads to a negative
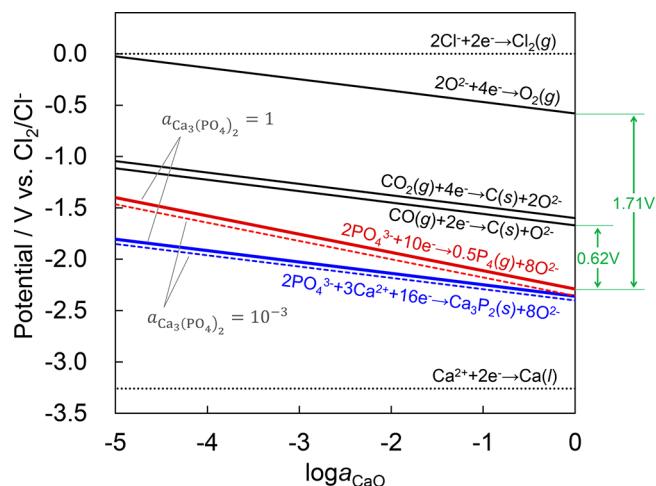
Figure 1. Relationships between occurring potentials of some redox reactions and activity of CaO in the molten bath of $CaCl_2$-$Ca_3(PO_4)_2$ at 850 °C. Activities of species other than CaO (or O^{2-}) and $Ca_3(PO_4)_2$ (or PO_4^{2-}) are taken as unity. $a_{CaO} = a_{O^{2-}}$, $a_{Ca_3(PO_4)_2} = a_{PO_4^{3-}}^2$.

deviation for all reactions. The result implies the thermodynamic feasibility of phosphorus extraction from dissolved phosphate in molten $CaCl_2$ by electrochemical deoxidation. The phosphorus extraction potential is within the electrochemical window of molten $CaCl_2$ and fairly positive than the calcium deposition potential.

An electrolysis cell can be designed to integrate phosphorus extraction on the cathode and CO evolution on a carbon anode. The total reaction is the combination of reactions 7 and 23.

$$2PO_4^{3-} + 5C(s) \rightarrow 0.5P_4(g) + 5CO(g) + 3O^{2-} \quad (25)$$
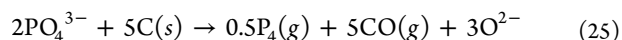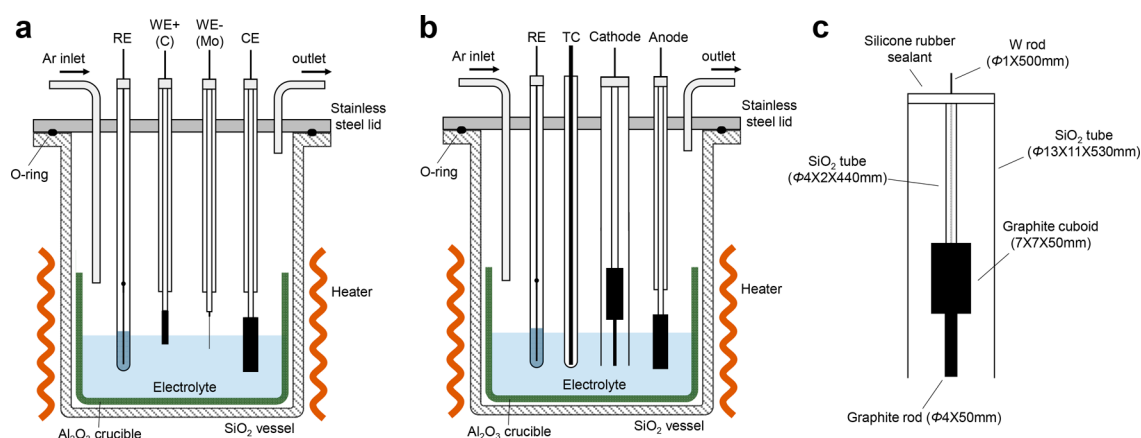
which can be written as

Figure 2. Schematic illustrations of experimental setup in this paper. (a) Experimental setup for cyclic voltammetry measurement. (b) Experimental setup for electrolysis. (c) Structure of the cathode used for electrolysis. (RE: Reference electrode; CE: counter electrode; WE+: working electrode for scanning toward positive potentials; WE-: working electrode for scanning toward negative potentials; TC: K-type Thermocouple).

$$Ca_3(PO_4)_2 \text{ (in } CaCl_2) + 5C(s)$$
$$\rightarrow 0.5P_4(g) + 5CO(g) + 3CaO \text{ (in } CaCl_2) \quad (26)$$
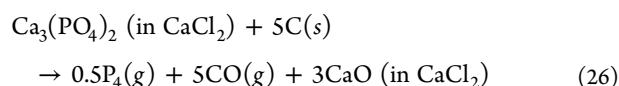
The minimum required cell voltage ($E_{(26)}^{min}$) to drive reaction 26 at 850 °C is

$$E_{(26)}^{min} = 0.62 + 0.068 \log a_{CaO} - 0.022 \log a_{Ca_3(PO_4)_2} \quad (27)$$

$E_{(26)}^{min}$ at standard state is 0.62 V, roughly half to the minimum required cell voltage for water electrolysis (1.23 V) at room temperature. Equation 27 indicates that decreasing CaO activity and increasing $Ca_3(PO_4)_2$ activity in the molten salt would decrease the required voltage to drive reaction 26 and benefit lowering energy consumption. However, since the progress of reaction 26 would consume $Ca_3(PO_4)_2$ and generate CaO in the molten salt, the required voltage is expected to increase with the gradual increase in CaO activity and decrease in $Ca_3(PO_4)_2$ activity.

It is possible to employ an electroconductive and oxidation-resistive material as the anode to evolve oxygen instead of carbon oxides. The total reaction is the combination of reactions 7 and 22

$$Ca_3(PO_4)_2 \text{ (in } CaCl_2)$$
$$\rightarrow 0.5P_4(g) + 5O_2(g) + 3CaO \text{ (in } CaCl_2) \quad (28)$$
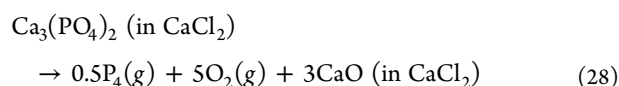
The minimum required cell voltage ($E_{(28)}^{min}$) to drive reaction 28 at 850 °C is

$$E_{(28)}^{min} = 1.71 + 0.068 \log a_{CaO} - 0.022 \log a_{Ca_3(PO_4)_2} \quad (29)$$

Oxygen evolution inert anode has the advantage in avoid carbon emission; yet, the required electrical energy is approximately three times as much. Development of oxygen evolution inert anode used in molten salt system is one of the research frontiers in the field of electrometallurgy.[23−25]

Figure 1 also indicates that the occurring potentials of phosphorus extraction is approaching the potential of phosphide formation with the increase in CaO activity. It is considered that phosphorus and phosphide may form simultaneously under some circumstances during the electrolysis, especially when the molten salt becomes more saturated with CaO.

■ EXPERIMENTAL SECTION

An experiment was conducted to verify the feasibility of phosphorus extraction by electrolyzing the molten bath of $CaCl_2$-$Ca_3(PO_4)_2$ at 850 °C.

Materials. An Al_2O_3 crucible (o.d. 90 × i.d. 80 × height 140 mm, Nikkato Corp.) containing 300 g of reagent grade $CaCl_2$ (Fujifilm Wako Pure Chemical Corp.) was set inside a sealed SiO_2 vessel (o.d. 135 × i.d. 127 × height 400 mm) under a dry argon atmosphere (150 mL min^{-1}) at 850 °C. $CaCl_2$ was kept under a vacuum at 180 °C for 72 h and 500 °C for 24 h to remove moisture prior to experiment. Reagent grade $Ca_3(PO_4)_2$ (99%, monoclinic, Fujifilm Wako Pure Chemical Corp.) was used as the phosphorus precursor.

Methods. Electrochemical experiments were conducted by using the potentiostat (HZ-7000 series, model HAG1232m, Hokuto Denko Corp.). Cyclic voltammetry (CV) was conducted in the three-electrode manner with a scan rate of 0.5 V s^{-1}. The experimental setup is shown in Figure 2a. The reference was an Ag^+/Ag electrode prepared by immersing a silver wire (99.9%, diameter 1 mm, Nilako Corp.) into $CaCl_2$ containing 0.5 mol % AgCl (99%, Fujifilm Wako Pure Chemical Corp.) in a mullite tube (o.d. 6 × i.d. 4 × height 500 mm, Nikkato Corp.). The counter electrode was a graphite rod (99.99%, 10 mm diameter, 3 cm melt immersed, Nilako Corp.). When scanning toward potentials negative than the reference electrode, the working electrode was a molybdenum wire (99.95%, 0.2 mm diameter, 5 mm melt immersed, Nilako Corp.). When scanning toward positive potentials, the working electrode was a graphite rod (99.99%, 3 mm diameter, 3 mm melt immersed, Nilako Corp.).

After CV was conducted in pure $CaCl_2$, $Ca_3(PO_4)_2$ of 6 g was added into the melt to make the solution of $CaCl_2$-$Ca_3(PO_4)_2$ (2 mass %), and CV was conducted again. The potential of the reference electrode was checked by Cl_2/Cl^- potential estimated by CV. All the potentials are given with reference to the Cl_2/Cl^- potential.

Constant potential electrolysis in $CaCl_2$-$Ca_3(PO_4)_2$ (2 mass %) was conducted at −2.48 V (vs Cl_2/Cl^-) in the three-electrode manner. The experimental setup is shown in Figure 2b. Design of the cathode is shown in Figure 2c. It is expected that the electrolyzed product would accumulate on the inner wall in the upper part of the cathode. The melt immersed depth of cathode is 3 cm. The reference was the same as in the CV test. The anode was the counter electrode used in the CV test. Temperature distribution on the cathode was measured by a K-type thermocouple.

Characterization. The electrolyzed product was recovered by disassembling the cathode and washing with distilled water and preserved in distilled water. The morphology was observed by a digital microscope (Dino-Lite Premier AM4113T, AnMo Corp.) and scanning electron microscope (SEM, VE-8800, Keyence Corp.). The composition was determined by energy-dispersive X-ray spectroscopy

(EDX, DAX Genesis APEX2, AMETEK Co., Ltd.) with beam accelerating voltages ranging from 3 kV to 15 kV.

RESULTS AND DISCUSSION

Cyclic Voltammogram. The feasibility of reducing dissolved $Ca_3(PO_4)_2$ in molten salt were verified by conducting cyclic voltammetry. As shown in Figure 3, the cyclic voltammo-
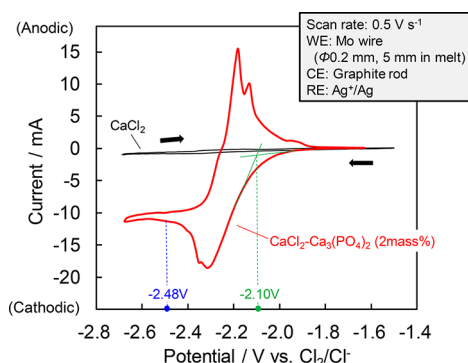

Figure 3. Cyclic voltammograms at a Mo wire (0.2 mm diameter, 5 mm melt immersed) in molten $CaCl_2$ and $CaCl_2$-$Ca_3(PO_4)_2$ (2 mass %) in an Al_2O_3 crucible at 850 °C. All are the second cycle. The potential scan rate is 0.5 V s^{-1}.

gram on a Mo wire electrode is generally flat in pure $CaCl_2$ (black curve). After adding 2 mass % of $Ca_3(PO_4)_2$, two cathodic peaks (-2.32 V and -2.35 V vs Cl_2/Cl^-) and two anodic peaks (-2.13 V and -2.18 V) appear clearly (red curve). It is considered that $Ca_3(PO_4)_2$ dissolves in molten $CaCl_2$ to form soluble phosphate ions such as PO_4^{3-}. The cathodic peaks correspond to reduction of phosphate ions, and anodic peaks to reoxidation of reduced products. In the subsequent constant potential electrolysis, the reduction peaks were proven to be formation of elemental phosphorus gas. Since the potential scan rate is as high as 0.5 V s^{-1}, most of the produced phosphorus can stay on the electrode. Accordingly, the anodic currents of reoxidation of phosphorus can be observed. The occurring potential of phosphorus extraction from phosphate ions read from Figure 3 is -2.10 V (potential at the intersection of the extrapolation tangent of the steep current and the baseline). Assuming that $Ca_3(PO_4)_2$ shows an ideal behavior in the molten salt bath due to the low concentration ($a_{Ca_3(PO_4)_2} = X_{Ca_3(PO_4)_2} = 0.006$; X means mole fraction), and substitute $E_{PO_4^{3-}/P_4} - E_{Cl_2/Cl^-} = -2.10$ V into eq 13, the activity of CaO is calculated to be $a_{CaO} = 0.046$, which is a reasonable value. In order to achieve an integrated understanding of the reducing behavior of phosphate ions, it will be an important subject to study the thermodynamic properties of molten $CaCl_2$-$Ca_3(PO_4)_2$, which were rarely reported in the past.

Preparation of Phosphorus by Electrolysis. Following the findings by CVs, constant potential electrolysis was conducted at -2.48 V (vs Cl_2/Cl^-) in molten $CaCl_2$-$Ca_3(PO_4)_2$ (2 mass %) at 850 °C in a three-electrode cell (Figure 2b). In order to clarify the products of the reduction peaks in Figure 3, a potential slightly negative than the potentials of reduction peaks was chosen for electrolysis.

Figure 4a,b shows the photos of a typical cathode before and after electrolysis for 7 h, respectively. Accumulation of yellow and red substances in the inner wall of the SiO_2 tube in the upper part was observed during electrolysis. These substances were later identified to be elemental phosphorus by SEM and EDX.
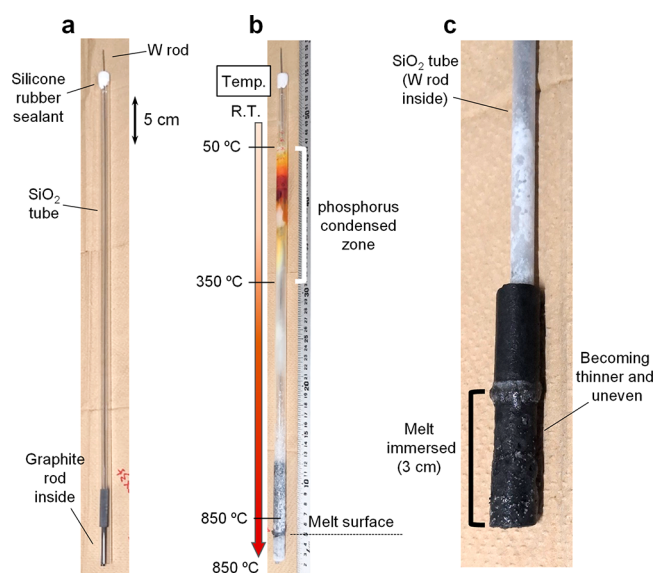

Figure 4. Photos of electrodes before and after electrolysis at -2.48 V (vs Cl_2/Cl^-) for 7 h in molten $CaCl_2$-$Ca_3(PO_4)_2$ (2 mass %) at 850 °C. (a) A cathode before electrolysis. (b) A cathode after electrolysis (electrolyzed phosphorus was condensed in the inner wall), labeled with temperature distribution when the cathode was in the furnace. (c) A graphite rod anode after electrolysis.

The amount of accumulation was generally in proportion to the electrolysis time in our experiments.

Since the reaction temperature (850 °C) is much higher than the boiling point of phosphorus [280 °C [3]], phosphorus vapor [$P_4 (g)$] is formed and evolved on the cathode. Phosphorus has two major allotropes, white phosphorus and red phosphorus. It is considered that white phosphorus is formed by electrolysis at the very beginning. Because of the high temperature in the furnace, some earlier formed white phosphorus gradually transforms to red phosphorus during the process.[26] The appearance of white phosphorus containing a small amount of red phosphorus turns to yellow. Therefore, the electrolyzed products exhibit both appearances of red and yellow.

The cathodic current density is about -0.1 A cm^{-2} for the entire process, except for the last 1 h, as shown in Figure 5. The decreased current may be due to the consumption of phosphate ions and the accompanying change of phosphorus extraction potential. The total quantity of electric charge is 9489.4 C, which corresponds to formation of 0.610 g of phosphorus assuming 100% current efficiency for reaction 5. Since the active surface
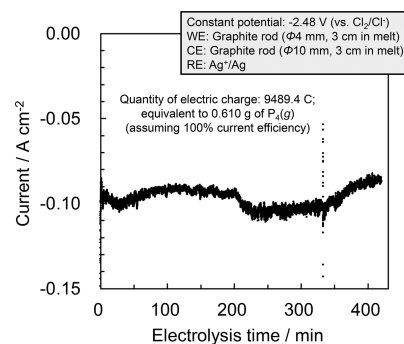

Figure 5. Variation of current density during electrolysis at -2.48 V (vs Cl_2/Cl^-) for 7 h in molten $CaCl_2$-$Ca_3(PO_4)_2$ (2 mass %) at 850 °C.

area of the cathode in melt is ca. 3.9 cm^{-2}, the maximum production rate of phosphorus can be calculated to be 0.22 kg m^{-2} h^{-1} in the present case. However, because of the difficulty in measuring precisely the weight of the reduced phosphorus, which is highly reactive in air, the actual current efficiency and production rate in the experiment are unknown.

After electrolysis, a small amount of dark-brown deposits was found on the surface of the graphite rod cathode. When immersed in distilled water, the deposits burned with a flame and released a garlic smell. We consider that $Ca_3P_2(s)$ was formed as a side reaction product at the later stage of electrolysis when the molten salt became poor in PO_4^{2-} [or $Ca_3(PO_4)_2$] and rich in O^{2-} (or CaO), as explained in the previous section of thermodynamic analysis. $Ca_3P_2(s)$ reacts with water rapidly to form phosphine $[PH_3(g)]$, which has a garlic smell and burns in air spontaneously. This result suggests that a dynamic control in potential and molten salt composition during electrolysis is indispensable for a high efficiency in practice. The graphite rod cathode itself shows no change after electrolysis, indicating that carbon does not participate in the cathodic reactions.

Characterization of Electrolysis Product. The electrolyzed phosphorus was recovered after disassembling the cathode and washing with distilled water. Figure 6a shows a microscope
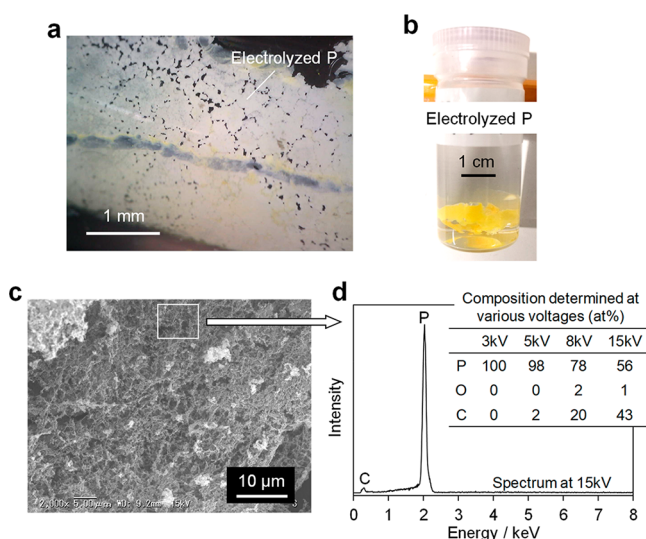

Figure 6. Observation and characterization of phosphorus (yellow appearance) obtained by electrolysis at −2.48 V (vs Cl_2/Cl^-) for 7 h in molten $CaCl_2$-$Ca_3(PO_4)_2$ (2 mass %) at 850 °C. (a) Electrolyzed phosphorus condensed on the wall of the SiO_2 tube. (b) Electrolyzed phosphorus preserved in water in a glass bin. (c) SEM image of the electrolyzed phosphorus. (d) EDX spectrum of the electrolyzed phosphorus and composition determined at various electron beam accelerating voltages.

photograph of electrolysis products condensed on the wall of the SiO_2 tube. Figure 6b shows the recovered phosphorus preserved in water in a glass bin. It is waxy and the appearance is yellow. SEM observation indicates that these white or yellow substances are an accumulation of submicron-sized particles (Figure 6c). EDX analysis confirmed that the products are elemental phosphorus (Figure 6d). The particles should be even finer at the moment of condensation because they have experienced a process of size growth before recovery.

The electrolyzed phosphorus is believed to have a high purity, although precise chemical analysis had not been conducted yet. Impurities were not detected by EDX analysis except for trace

oxygen and a certain amount of carbon. Oxygen is considered to originate from the inevitable oxidation when exposing the sample in air. Carbon was detected because a carbon adhesive tape was used to mount the powdery sample on a stage. In fact, carbon detection was enhanced by increasing the electron beam accelerating voltage of SEM (Figure 6d), which indicates the penetration of electron beam in the powdery product. In our previous studies,[18,27] very high purity silicon (>99.9%) was prepared by electrolysis in molten $CaCl_2$. According to the similarities in raw materials and experimental setup, phosphorus obtained in this study should also have a high purity.

A piece of phosphorus with a yellow appearance exposed in air turned into plumes of white smoke (phosphorus oxides) and vanished in seconds. The oxidation process was recorded as shown in Movie S1. This is the evidence that white phosphorus had been formed by electrolysis. The high reactivity in air of the white phosphorus is also the major reason why we failed to measure the current efficiency and conduct the chemical analysis with our existing facilities. On the contrary, the obtained phosphorus with a red appearance is stable in air. Figure 7 shows
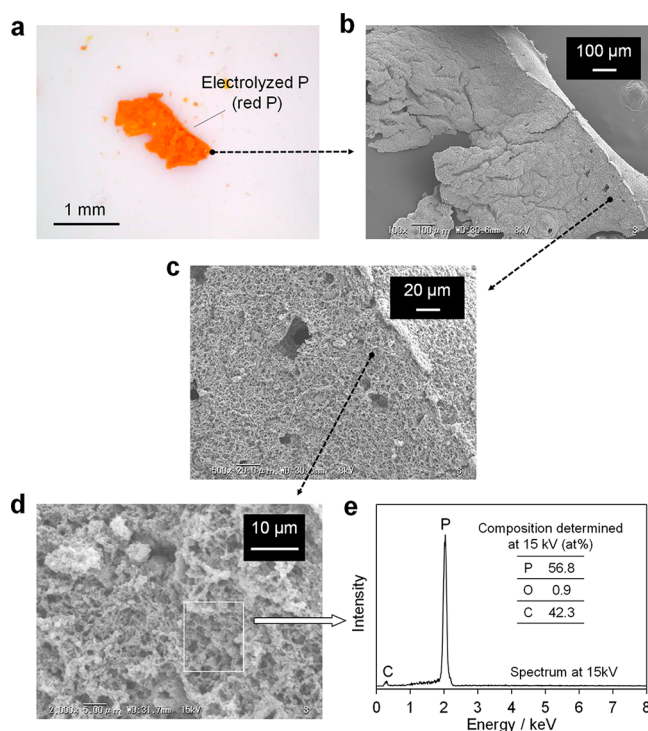

Figure 7. Observation and characterization of phosphorus (red appearance) obtained by electrolysis at −2.48 V (vs Cl_2/Cl^-) for 7 h in molten $CaCl_2$-$Ca_3(PO_4)_2$ (2 mass %) at 850 °C. (a) Photograph of a piece of electrolyzed phosphorus (red) exposed in air. (b) SEM image of the sample in a. (c) Magnified SEM image of the location in b. (d) Magnified SEM image of the location in c. (e) EDX spectrum and composition determined at 15 kV of the location in d.

the observation and characterization of red phosphorus. Although not very noticeable, particle size (Figure 7d,e) is slightly larger than that of the white phosphorus (Figure 6c), while their compositions determined by EDX are similar.

Formation Mechanism. Figure 8 illustrates the formation mechanism of phosphorus by electrolysis. The negative potential applied on the cathode drives the electrochemical deoxidation of phosphate ions to form gaseous phosphorus. Even though intermediate products may have been formed, the
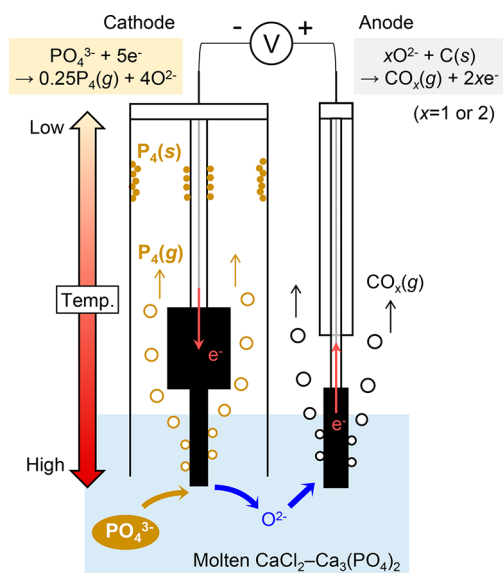
Figure 8. A schematic illustration of the formation mechanism of elemental phosphorus by electrolysis in molten $CaCl_2$-$Ca_3(PO_4)$.

Figure 9. Concept of a new process to produce white phosphorus from various phosphate-bearing precursors by electrolysis in molten $CaCl_2$. M^{x+} denotes possible impurity-bearing ions released from the precursor.

overall cathodic reaction could be described by reaction 5. Oxide ions liberated on the cathode diffuse toward the anode. Being soluble for phosphate and oxide ions is the essential character of molten $CaCl_2$ making it a suitable solvent in extracting phosphorus. The rate-limiting step for the whole process is likely to be either the diffusion of phosphate ions or the diffusion of oxide ions in the molten salt.

An apparent decrease in diameter and an uneven surface were observed for the graphite rod anode after electrolysis, as shown in Figure 4c. The anodic reaction is believed to be the formation of CO (g) or CO_2 (g) (reaction 23 or 24) which consumes graphite. Therefore, the total reaction can be written as reaction 26 given CO is formed.

After nucleation and growth, the phosphorus bubbles would detach from the cathode, rise to the melt surface, and leave the melt. A continuous generation of phosphorus by electrolysis is therefore realized, despite phosphorus being not electroconductive. The phosphorus vapor flowing through the SiO_2 tube upward is condensed as solid or liquid in the low temperature zone (roughly from 50 to 350 °C), which is basically consistent with the temperature range from melting point (44 °C) to boiling point (280 °C) of phosphorus [3].

Proposal of a New Phosphorus-Making Process. Our work has thus shown a simple method of extracting phosphorus from dissolved $Ca_3(PO_4)$ in molten $CaCl_2$ by electrolysis. Since $Ca_3(PO_4)$ is contained in phosphate rock as well as in phosphate-bearing wastes, this method is also applicable to recycle of phosphorus resource. Like from wastewater, phosphorus removal and recovery are always important environmental issues worldwide. Wastewater or sludge treatment by calcium-based chemicals simply precipitates calcium phosphates,[28,29] which can be used as the phosphorus precursor in our method. Steelmaking slag is a byproduct with a massive amount generated in steelmaking plants after steel dephosphorization. Producing white phosphorus from phosphate-enriched phase separated from steelmaking slag is also possible.[30,31]

Figure 9 illustrates the concept of a new process to produce white phosphorus from various phosphate-bearing precursors by electrolysis in molten $CaCl_2$. An ideal design for the electrolysis cell will have the cathode set at the bottom. Precursors processed
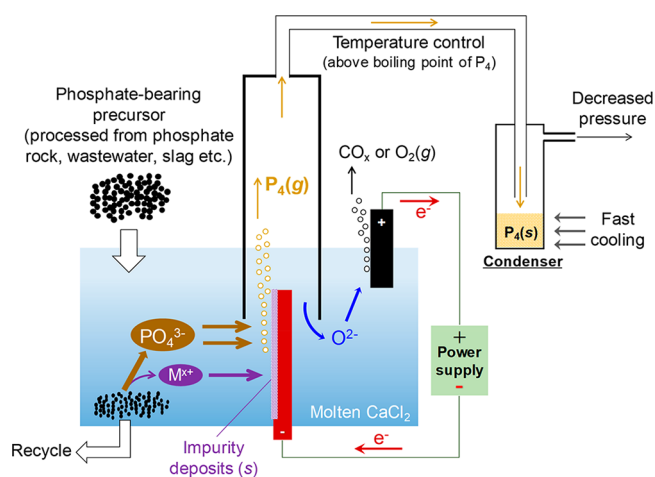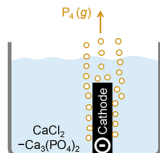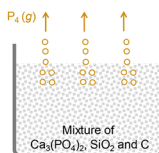
from phosphate rock, wastewater, or slag can be added into the cell from the top on one side. After the dissolution of phosphate ions from the solid precursor into the molten salt phase, electrolyzing the melt generates phosphorus vapor on the cathode, which would be induced to flow into a condenser for recovery. If impurity ions are also released from the precursor into the molten salt, controlling the electrolysis potential precisely will be useful to reduce phosphorus selectively. Reduction potential of phosphorus is more positive than that of most metals. Even if any impurity ions contained in the molten salt are reduced to form metals or phosphides during electrolysis, they would deposit on the cathode surface rather than contaminating the gaseous product, which would enable high-purity phosphorus to be produced. A continuous electrolysis would not be influenced by the deposits because metals or phosphides are electroconductive at high temperatures. Oxygen ions isolated from the phosphate ions are liberated as CO or CO_2 on a carbon anode (or O_2 on an inert anode). Evolution of Cl_2 on the anode can be avoided by controlling the electrochemical conditions, because evolution of CO or CO_2 on a carbon anode (or O_2 on an inert anode) is thermodynamically more favored. Solid residues, if any, can be recycled as the raw material in cement or steelmaking plants. Continuous operation of solid residues removal, precursor addition, and phosphorus recovery would enable a high productivity.

The newly proposed electrolysis route to extract white phosphorus is compared with the conventional carbothermic reduction route in Table 3. Several advantages could be estimated. Lowering temperature from 1500 to 850 °C would bring benefits such as easier operation, less contamination by impurities and decreased attrition rate of the equipment. Replacing coke by electricity as the reducing agent may decrease the materials loss as well as the byproducts emission. Moreover, the theoretical energy consumption of the electrolysis route is calculated to be 8.9 MWh per ton of phosphorus (method described in the Supporting Information), which is 17% less compared with the carbothermic reduction route [10.8 MWh $(ton-P)^{-1}$]. Therefore, it is expected that upgrading the technology of producing white phosphorus from carbothermic

Table 3. Comparison of Two Routes to Produce White Phosphurus. (a) Electrolysis Route (Newly Proposed) and (b) Carbothermic Reduction Route (Conventional Technology)[a]

	(a) Electrolysis	(b) Carbothermic reduction
Principle		
Major reaction	$2Ca_3(PO_4)_2$ (in $CaCl_2$) + $10C$ (s) $\rightarrow$ P_4 (g) + $10CO$ (g) + $6CaO$ (in $CaCl_2$)	$2Ca_3(PO_4)_2$ (s) + $10C$ (s) + $6\,SiO_2$ (s) $\rightarrow$ P_4 (g) + $10CO$ (g) + $6CaSiO_3$ (s)
Operational temperature	850 °C	1500 °C
Reducing agent	Electricity	Coke
Theoretical energy consumption	8.9 MWh (ton-P)$^{-1}$	10.8 MWh (ton-P)$^{-1}$

[a]Actual energy consumption of carbothermic reduction route[7,8] (using phosphate rock) is 14−18 MWh (ton-P)$^{-1}$. Energy required to heat the equipment or facility is not considered in the calculation. In the electrolysis route, $CaCl_2$ is regarded as a part of the equipment.

reduction to electrolysis may lead to a substantial improvement in simplicity, cleanness, and energy efficiency.

Although only 2 mass % of phosphate was used as the precursor in the demonstration experiment in this work, it is possible to increase the concentration to approximately 5 mass % at 850 °C.[20] The concentration can be increased further by raising the temperature upon the requirement in production rate. We acknowledge that there are a lot of scientific problems and technical difficulties to be solved before turning the concept into practice. It is our anticipation that an advanced phosphorus-making technology based on our work would eventually address the global challenge in phosphorus supply.

■ CONCLUSION

This work presents and demonstrates a new concept for producing white phosphorus by electrolysis of phosphate-containing molten salt. The molten salt system $CaCl_2$-$Ca_3(PO_4)_2$ was studied. $Ca_3(PO_4)_2$ dissolves in molten $CaCl_2$ to form a solution containing diffusible phosphate ions, which are confirmed to be electrochemically reducible. Cyclic voltammetry conducted in molten $CaCl_2$-$Ca_3(PO_4)_2$ (2 mass %) shows that phosphorus can be extracted at potentials negative than −2.10 V (vs Cl_2/Cl^-) at 850 °C. Accordingly, electrolyzing the molten bath at a constant potential of −2.48 V (vs Cl_2/Cl^-) results in continuous formation of phosphorus vapor on the cathode and carbon oxides on the carbon anode. A sustainable process to produce white phosphorus from phosphate-bearing precursors by electrolysis in molten $CaCl_2$ is thus proposed. This work may lead to the start of a sustainable chapter for the phosphorus industry.

■ ASSOCIATED CONTENT

ⓈI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.0c04796.

Theoretical energy consumption for the newly proposed electrolysis route and the conventional carbothermic reduction route are calculated according to thermochemical data (Table S1) (PDF)

The oxidation process of electrolyzed phosphorus in air was recorded as a movie by using a digital microscope (Movie S1) (MP4)

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Author Contributions

X.Y. conceived the idea, designed and conducted the experiment and analysis, interpreted the data and wrote the manuscript. T.N. contributed to apparatus setup, discussed the data, and critically revised the manuscript.

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Slootweg, J. C. Sustainable Phosphorus Chemistry: A Silylphosphide Synthon for the Generation of Value-Added Phosphorus Chemicals. *Angew. Chem., Int. Ed.* **2018**, *57* (22), 6386−6388.

(2) Karapinar, B. China's export restriction policies: complying with 'WTO plus' or undermining multilateralism. *World Trade Review* **2011**, *10* (3), 389−408.

(3) Corbridge, D. E. C. *Phosphorus: Chemistry, Biochemistry and Technology*, 6th ed.; CRC Press, 2016; p 93.

(4) Readman, J. B. Process of Obtaining Phosphorus. U.S. Patent 417943, Dec. 24, 1889.

(5) Wang, Z.; Jiang, M.; Ning, P.; Xie, G. Thermodynamic modeling and gaseous pollution prediction of the yellow phosphorus production. *Ind. Eng. Chem. Res.* **2011**, *50* (21), 12194−12202.

(6) Readman, J. B. An account of the manufacture of phosphorus. Part I. *J. Soc. Chem. Ind., London* **1890**, *9* (2), 163−165.

(7) Kubo, H.; Matsubae, K.; Nagasaka, T. Present Status and Strategies for Resource Security of Zinc and Phosphorus. *Hyomen Gijutsu* **2015**, *66* (3), 86−90.

(8) Ma, H.; Liu, C.; Su, S.; Sun, H.; Liu, M. Phosphorus resource and sustainable development of phosphorus chemical industry in China. *Earth Science Frontiers* **2017**, *24*, 133−141.

(9) Gruber, B. A. Method for the Preparation of Pure Elemental Phosphorus. U.S. Patent 2955552 Dec. 20, 1960.

(10) Caton, R.; Freund, H. Polarography in Fused Alkali Metaphosphates. *Anal. Chem.* **1963**, *35* (13), 2103−2108.

(11) Laitinen, H.; Lucas, K. A study of the electro reduction of metaphosphate in molten LiCl-KCl eutectic. *J. Electroanal. Chem.* **1966**, *12* (5−6), 553−563.

(12) Franks, E.; Inman, D. The electroreduction of molten phosphates. *J. Electroanal. Chem. Interfacial Electrochem.* **1970**, *26* (1), 13−26.

(13) Callis, C. F.; Van Wazer, J. R.; Metcalf, J. S. Structure and properties of the condensed phosphates. IX. Viscosity of molten sodium phosphates. *J. Am. Chem. Soc.* **1955**, *77* (6), 1471−1473.

(14) Chen, G. Z.; Fray, D. J.; Farthing, T. W. Direct electrochemical reduction of titanium dioxide to titanium in molten calcium chloride. *Nature* **2000**, *407* (6802), 361−364.

(15) Nohira, T.; Yasuda, K.; Ito, Y. Pinpoint and bulk electrochemical reduction of insulating silicon dioxide to silicon. *Nat. Mater.* **2003**, *2* (6), 397−401.

(16) Jin, X.; Gao, P.; Wang, D.; Hu, X.; Chen, G. Z. Electrochemical preparation of silicon and its alloys from solid oxides in molten calcium chloride. *Angew. Chem., Int. Ed.* **2004**, *43* (6), 733−736.

(17) Ono, K.; Suzuki, R. O. A new concept for producing Ti sponge: Calciothermic reduction. *JOM* **2002**, *54* (2), 59−61.

(18) Yang, X.; Ji, L.; Zou, X.; Lim, T.; Zhao, J.; Yu, E. T.; Bard, A. J. Toward Cost-Effective Manufacturing of Silicon Solar Cells: Electrodeposition of High-Quality Si Films in a CaCl2-based Molten Salt. *Angew. Chem., Int. Ed.* **2017**, *56*, 15078−15082.

(19) Xiao, W.; Wang, D. The electrochemical reduction processes of solid compounds in high temperature molten salts. *Chem. Soc. Rev.* **2014**, *43* (10), 3215−3228.

(20) Epperlein, J.; Lehmann, H. A. Über die Beziehungen zwischen Chlorapatit und Chlorspodiosit im System CaCl2-Ca3(PO4)2. *Z. Chem.* **1973**, *13* (7), 261−261.

(21) Barin, I. *Thermochemical Data of Pure Substances*; VCH: Weinheim, Germany, 1989.

(22) Dobrokhotova, Z. V.; Zaitsev, A.; Zemchenko, M.; Litvina, A.; Mogutnov, B.; Yaschenko, S. Thermodynamic properties of calcium and barium phosphides. *J. Therm. Anal.* **1992**, *38* (5), 1113−1122.

(23) Allanore, A.; Yin, L.; Sadoway, D. R. A new anode material for oxygen evolution in molten oxide electrolysis. *Nature* **2013**, *497* (7449), 353.

(24) Pal, U. B.; Woolley, D. E.; Kenney, G. B. Emerging SOM technology for the green synthesis of metals from oxides. *JOM* **2001**, *53* (10), 32−35.

(25) Wang, D.; Xiao, W. Inert Anode Development for High-Temperature Molten Salts. In *Molten Salts Chemistry*; Lantelme, F.; Groult, H., Eds.; Elsevier: Oxford, 2013; pp 171−186. DOI: 10.1016/B978-0-12-398538-5.00009-3.

(26) Bachhuber, F.; von Appen, J.; Dronskowski, R.; Schmidt, P.; Nilges, T.; Pfitzner, A.; Weihrich, R. The extended stability range of phosphorus allotropes. *Angew. Chem., Int. Ed.* **2014**, *53* (43), 11629−11633.

(27) Yang, X.; Yasuda, K.; Nohira, T.; Hagiwara, R.; Homma, T. Cathodic Potential Dependence of Electrochemical Reduction of SiO2 Granules in Molten CaCl2. *Metall. Mater. Trans. E* **2016**, *3* (3), 145−155.

(28) Tang, S.; Yan, F.; Zheng, C.; Zhang, Z. Novel Calcium Oxide-Enhancement Phosphorus Recycling Technique through Sewage Sludge Pyrolysis. *ACS Sustainable Chem. Eng.* **2018**, *6* (7), 9167−9177.

(29) Zhang, Y.; Ma, H.; Lin, L.; Cao, W.; Ouyang, T.; Li, Y. Enhanced Simultaneous Nitrogen and Phosphorus Removal Performance by Anammox-HAP Symbiotic Granules in the Attached Film Expanded Bed Reactor. *ACS Sustainable Chem. Eng.* **2018**, *6* (8), 10989−10998.

(30) Yang, X.; Matsuura, H.; Tsukihashi, F. Condensation of P2O5 at the Interface between 2CaO SiO2 and CaO-SiO2-FeOx-P2O5 Slag. *ISIJ Int.* **2009**, *49* (9), 1298−1307.

(31) Kubo, H.; Matsubae-Yokoyama, K.; Nagasaka, T. Magnetic separation of phosphorus enriched phase from multiphase dephosphorization slag. *ISIJ Int.* **2010**, *50* (1), 59−64.