

The extraction of white phosphorus in molten salt

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ABSTRACT

White phosphorus (P_4) is a critical element in industry, but its current production from phosphate rock using the carbothermal reduction method raises significant environmental and health concerns. This pressing issue necessitates the development of new technologies that facilitate the sustainable production of P_4 . In response, my team is actively developing an innovative, coke-free approach for white phosphorus production. This method involves the dissolution of phosphate rock in molten CaCl_2 , followed by the extraction of P_4 through electrochemistry at relatively low temperatures. Moreover, this approach has the potential to utilize phosphate-bearing solid wastes as raw materials, further enhancing its environmental benefits. By employing this cutting-edge technique, we aim to revolutionize the phosphorus chemical industry towards greener and more sustainable practices. This paper provides evidence of the feasibility and effectiveness of our proposed approach.

INTRODUCTION

White phosphorus (P_4) is the starting material for various critical chemicals, such as phosphoric acids, chlorides, sulfides and phosphides. The global demand for P_4 has been steadily increasing in recent years. However, the P_4 -manufacturing industry is facing significant challenges as the production process is highly energy-intensive and environmentally harmful. The supply of P_4 is susceptible to national trade policies, further complicating its availability in the market. Consequently, securing a stable supply of P_4 has become an urgent concern for many countries.

The industrial production of P_4 involves heating a mixture of phosphate rock [$\text{Ca}_5(\text{PO}_4)_3\text{F}$], sand (SiO_2) and coke (C) in an electric furnace at around $1500\text{ }^\circ\text{C}$. This energy-intensive process, depicted in Fig. 1(a), consumes a substantial amount of electricity ($13.5\sim 15\text{ MWh}$ per ton of P_4) due to the highly endothermic nature of the carbon-driven reduction of phosphate. Ensuring product quality is challenging as the high temperatures make the process susceptible to impurity contamination, necessitating additional purification steps for high-purity product production. Furthermore, the emission of significant quantities of hazardous byproducts poses severe environmental concerns.

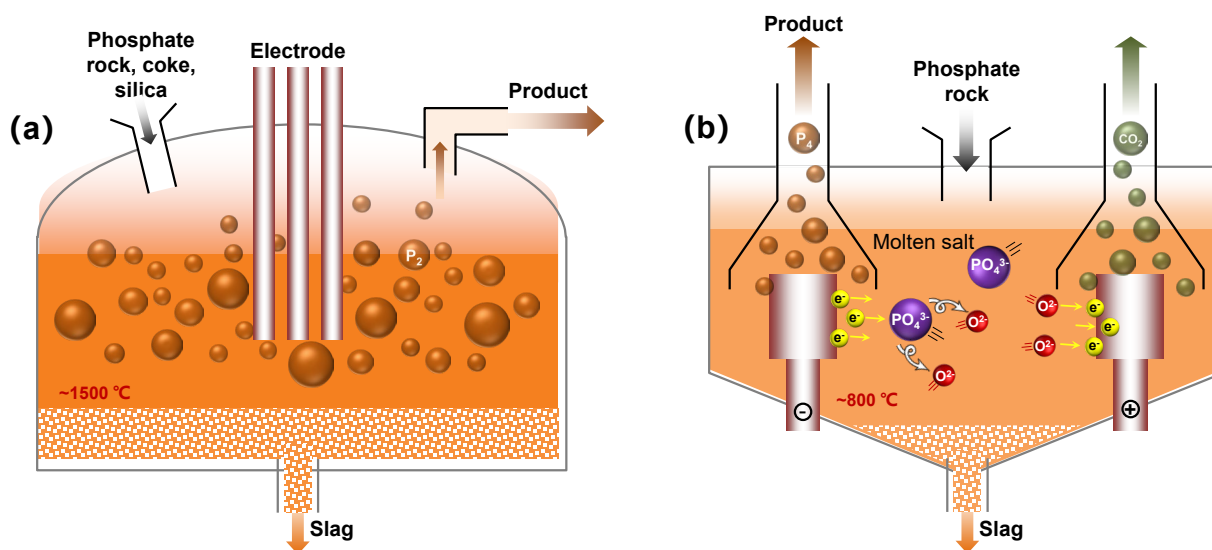


FIG 1 – Illustration of white phosphorus production processes: (a) the carbothermal reduction process and (b) the electrochemical reduction process.

The advancement of P_4 -manufacturing technology is crucial for sustainable development. In this study, we present a novel process for producing P_4 (Yang and Nohira, 2020; Liu et al., 2024), as illustrated in Fig. 1 (b). This innovative process involves dissolving phosphate rock in molten $CaCl_2$, followed by the electrochemical extraction of P_4 . Notably, this approach eliminates the need for coke and operates at a lower temperature of approximately $850\text{ }^\circ\text{C}$. As a result, the electrochemical method is expected to offer substantial advantages over the traditional carbothermal process, particularly in terms of simplicity and cleanliness. This paper demonstrates the feasibility and effectiveness of our proposed approach.

EXPERIMENT

Molten $CaCl_2$ was employed as the solvent and electrolyte. Pure $Ca_5(PO_4)_3F$ and natural phosphate rock (mined in Hubei, China) were added into molten $CaCl_2$ at $850\text{ }^\circ\text{C}$, respectively. Figure 2(a) shows the setup used to study the dissolution behavior of $Ca_5(PO_4)_3F$ or natural phosphate rock in molten $CaCl_2$. The experiment was performed in a crucible furnace. The melts sampled at regular time intervals by dipping an Al_2O_3 rod into the melt bath were analysed by ICP-MS to reveal the concentration of soluble phosphorus.

Electrochemical experiments were conducted in the melt after dissolving 20 g of phosphate rock in 300 g of molten $CaCl_2$ for 48 h at $850\text{ }^\circ\text{C}$. Cyclic voltammetry (CV) and electrolysis were conducted in a three-electrode manner. The reference electrode (RE) was an Ag^+/Ag electrode prepared by immersing an Ag wire in $CaCl_2$ containing 0.5 mol% $AgCl$ in a SiO_2 tube. A graphite rod (dia. 5 mm) enclosed by a quartz tube was used as the cathode and anode, which were immersed in the melt to a depth of 25 mm. The cathodic product after dissolving in CS_2 was tested by 600 MHz Solution NMR Spectrometer. The anodic gas was analyzed by Gas Chromatography.

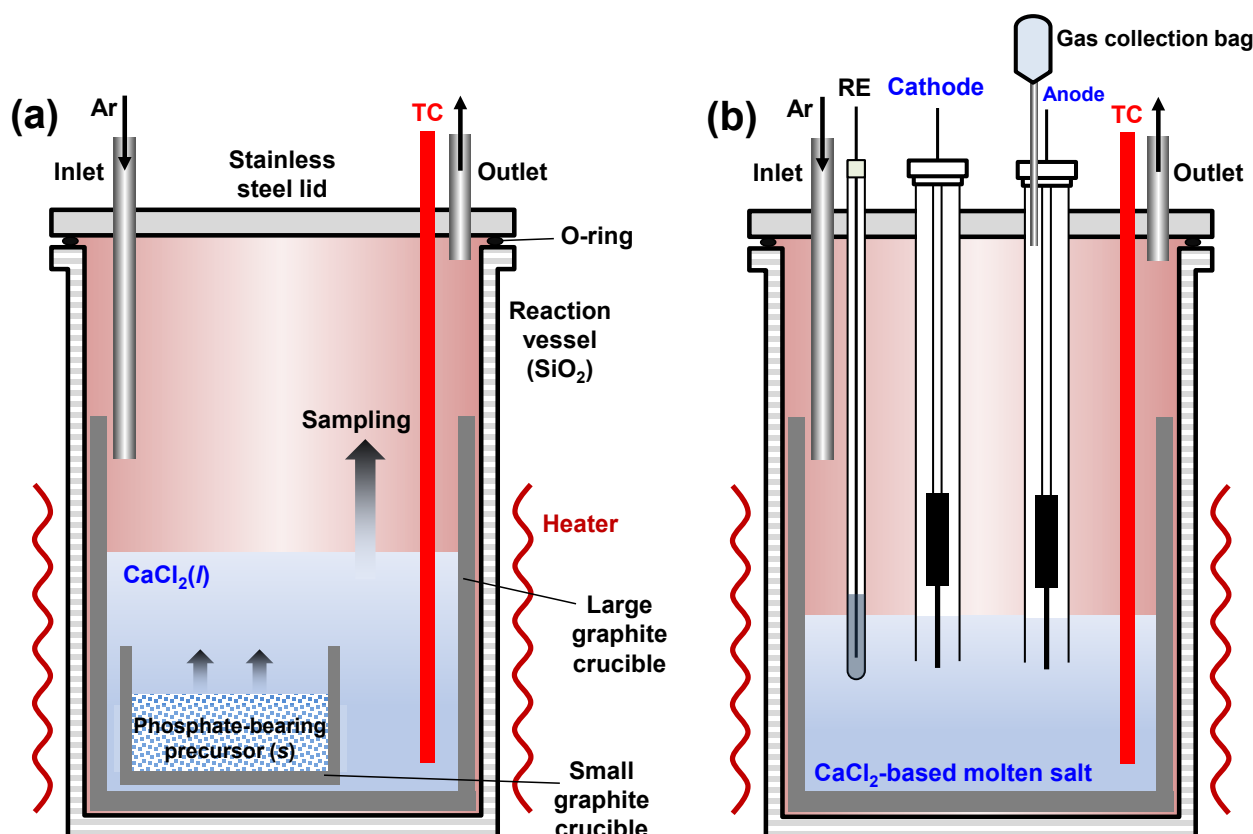


FIG 2 – Schematic diagram of experimental setups for (a) dissolution of $Ca_5(PO_4)_3F$ or phosphate rock in molten $CaCl_2$ and (b) electrochemical tests and P_4 extraction.

RESULTS AND DISCUSSION

In Fig. 3(a), the dissolution profiles of P from excessive phosphate rock in 300 g of molten CaCl₂ at different temperatures are presented. The results indicate that the concentrations of P in the melt increase rapidly and reach a plateau in less than 10 minutes, suggesting a fast and efficient dissolution process. The plateau values represent the solubility of P at each temperature, as they are lower than the theoretical concentration of P assuming complete dissolution of P in phosphate rock. The solubility of P is observed to increase with temperature. It should be noted that, in comparison to the dissolution of Ca₅(PO₄)₃F, the dissolution rate of P from phosphate rock is evidently higher, while the solubility is slightly lower. This difference can be attributed to the presence of impurities in the phosphate rock.

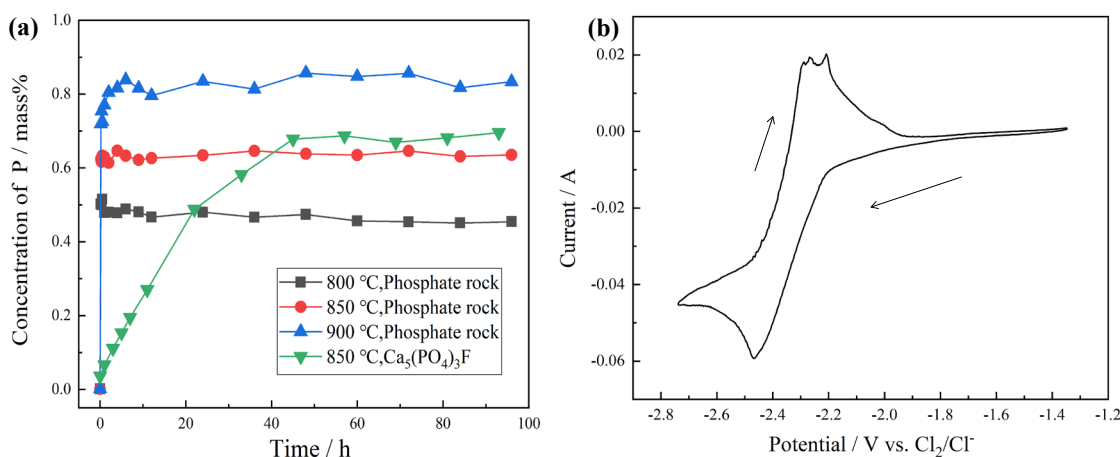
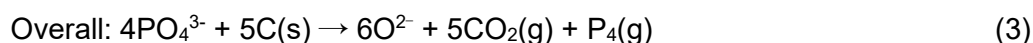
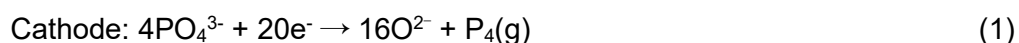


FIG 3 – (a) Dissolution profiles of P from phosphate rock and Ca₅(PO₄)₃F in molten CaCl₂ at various temperatures. (b) Cyclic voltammograms at a graphite rod electrode (dia. 3 mm, immersion depth 1 mm) in 300 g of molten CaCl₂ after dissolving 20 g of phosphate rock for 48 h at 850 °C.

Fig. 3(b) shows the cyclic voltammograms in the melt. Considering the electrical resistance of the melt, 70% IR compensation was applied. Cathodic currents increase at potentials negative than -2.0 V (vs. Cl₂/Cl⁻), which is attributed to the electrochemical reduction of PO₄³⁻. Subsequent investigations confirm that the product is P₄. A single cathodic peak can be clearly observed in most cases, suggesting that the electrochemical reduction of PO₄³⁻ can be approximated as a one-step (five-electron transfer) reduction process. The anodic peaks observed in the CV curves correspond to the oxidation of newly formed P₄ adhered on the cathode surface. The presence of multiple anodic peaks suggests that the oxidation process is more complex than the reduction process and may involve several intermediate products and electron transfer steps.

Following the cyclic voltammetry test, constant current electrolysis was conducted. Fig. 4(a) shows the photographs of the upper section of the cathode after electrolysis at -0.1 A cm⁻² for 10 h. Yellow substance condensed on the inner wall of the quartz tube was confirmed to be P₄ by 31P NMR analysis. Chemical analysis indicates that the obtained P₄ product through molten salt electrolysis is of significantly higher purity compared to the industrial-grade commercial product produced by the carbothermal reduction process.

Figure 4(b) shows the chromatograms of the anodic gas collected at different moments during the electrolysis. Both CO and CO₂ were identified in the anodic gas and the quantitative analysis showed that CO₂ was the dominant one. These results suggest that the following electrode reactions occur during electrolysis:



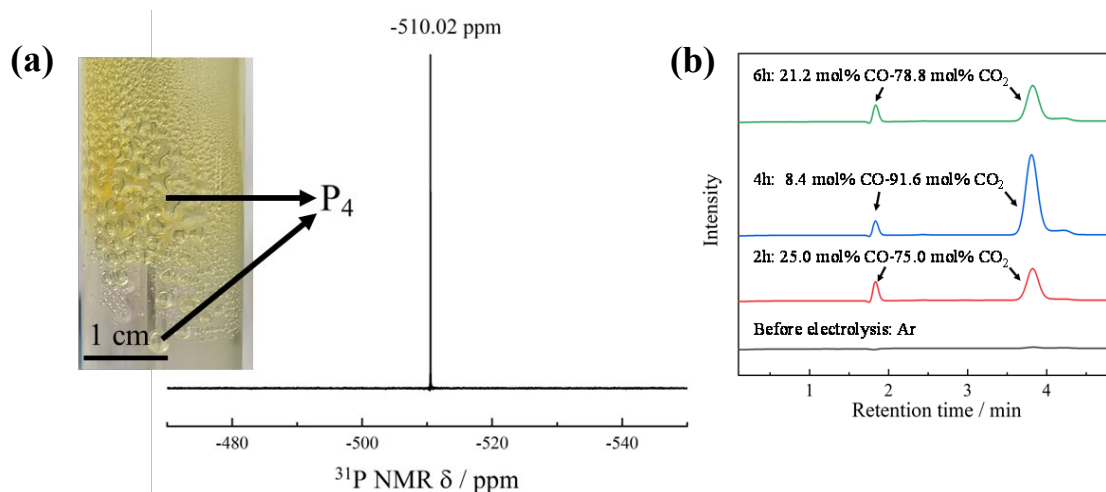


FIG 4 – (a) Photograph of the upper section of the quartz tube enclosing the cathode and ^{31}P NMR spectrum of the product after electrolysis at -0.1 A cm^{-2} for 10 h in the melt after dissolving 20 g of phosphate rock in 300 g of molten CaCl_2 for 24 h at $850 \text{ }^\circ\text{C}$. (b) Chromatograms of three anodic gas samples collected at different moments during the electrolysis and pure Ar

CONCLUSIONS

This work demonstrates a more environmentally friendly and efficient approach for extracting white phosphorus from phosphate rock through molten salt electrolysis. In this process, phosphate rock dissolves in molten CaCl_2 , allowing the soluble PO_4^{3-} to be electrochemically reduced. Notably, the operating temperature required for producing white phosphorus is only $850 \text{ }^\circ\text{C}$, which is significantly lower than that required in the conventional carbothermal reduction process. Additionally, white phosphorus produced through molten salt electrolysis exhibits a higher purity level compared to the industrial-grade commercial product obtained through carbothermal reduction. The electrochemical process also shows decreased electricity and carbon consumption. These findings underscore the potential of the electrochemical reduction process as a future method for extracting high-purity white phosphorus.

REFERENCES

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