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Communications

$V_2(PO_4)_3$: A Novel NASICON-Type Vanadium Phosphate Synthesized by Oxidative Deintercalation of Sodium from $Na_3V_2(PO_4)_3$

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There is considerable current interest in solid materials that can reversibly intercalate atomic species at low temperatures in view of the potential application of such solids in several fields including synthesis of new materials, battery electrodes, electrochromic displays, and chemical sensors.[1] A prototypical example of such a system is Li_xTiS_2, where lithium is incorporated reversibly in the van der Waals gap of the layered host structure.[2] Several transition-metal oxides of both layered and tunnel structures have been examined toward redox insertion/extraction reactions of lithium and other alkali metals.[1,3] Among these, vanadium oxides are especially attractive as hosts toward atom insertion reactions because of the accessibility of oxidation states ranging from III to V under normal experimental conditions. Most of the vanadium oxides investigated so far in such reactions consist of tunnel or layered structures built up of vanadium–oxygen polyhedra.[1a] An exception[4] is $VOPO_4{\cdot}2H_2O$, which crystallizes in a layered structure formed by linking of VO_6 octahedra and PO_4 tetrahedra. Besides $VOPO_4{\cdot}2H_2O$, many vanadium-containing oxides formed by VO_6 octrahedra and PO_4 and such other tetrahedra giving rise to tunnel or skeleton structures are known.[5] We envisaged that it should be possible to carry out reversible redox insertion/extraction reactions with such solids. In this communication, we report one such instance which enabled us to synthesize a novel vanadium phosphate, $V_2(PO_4)_3$, by oxidative extraction of sodium from the NASICON-like[5a] $Na_3V_2(PO_4)_3$. We also show that $V_2(PO_4)_3$, so prepared, where the interstitial channel sites of the NASICON structure are empty, is a novel host material for insertion of electropositive atoms such as lithium and hydrogen, by synthesizing $Li_xV_2(PO_4)_3$ and $H_3V_2(PO_4)_3$ starting from $V_2(PO_4)_3$.

We have chosen $Na_3V_2(PO_4)_3$ to investigate deintercalation of sodium for the following reasons: It has the NASICON $[Na_3Zr_2PSi_2O_{12}]$ framework wherein the sodium ions are known to move fast in the interstitial space.[6] The presence of vanadium in the III oxidation state in $Na_3V_2(PO_4)_3$ would permit oxidative deintercalation of sodium by common oxidizing agents such as the halogens.[3a]

$Na_3V_2(PO_4)_3$ was prepared by reacting Na_2CO_3, $(NH_4)H_2PO_4$, and V_2O_5 in stoichiometric proportion at 600–900 °C in a hydrogen atmosphere for 24 h, after a preliminary heating of the mixture at 300 °C for 12 h. Powder X-ray diffraction pattern of the sample (Figure 1a) and the unit cell parameters derived therefrom (Table I) agreed with the values reported[5a] for $Na_3V_2(PO_4)_3$. Moreover, the oxidation state of vanadium determined by redox potentiometric titration using Ce(IV) as the oxidant

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(1) See, for example: (a) Murphy, D. W.; Christian, P. A. *Science* **1979**, *205*, 651. (b) Whittingham, M. S., Jacobson, A. J., Eds. *Intercalation Chemistry*; Academic Press: New York, 1982. (c) Whittingham, M. S. *MRS Bull.* **1989**, *Sept*, 31–38.

(2) Whittingham, M. S. *Prog. Solid State Chem.* **1978**, *12*, 41–99.

(3) (a) Wizansky, A. R.; Rauch, P. E.; Disalvo, F. J. *J. Solid State Chem.* **1989**, *81*, 203. (b) Geselbracht, M. J.; Richardson, T. J.; Stacy, A. M. *Nature* **1990**, *345*, 324. (c) Manthiram, A.; Goodenough, J. B. *J. Solid State Chem.* **1987**, *71*, 349. (d) Nadiri, A.; Le Flem, G.; Delmas, C. *J. Solid State Chem.* **1988**, *73*, 338. (e) Vidyasagar, K.; Gopalakrishnan, J. *J. Solid State Chem.* **1982**, *42*, 217. (f) Subba Rao, G. V.; Varadaraju, U. V.; Thomas, K. A.; Sivasankar, B. *J. Solid State Chem.* **1987**, *70*, 101.

(4) Jacobson, A. J.; Johnson, J. W.; Brody, J. F.; Scanlon, J. C.; Lewandowski, J. T. *Inorg. Chem.* **1985**, *24*, 1782.

(5) (a) Delmas, C.; Olazcuaga, R.; Cherkaoui, F.; Brochu, R.; Le Flem, G. *C.R. Acad. Sc. Paris. Ser. C* **1978**, *287*, 1969. (b) Lii, K. H.; Wang, Y. P.; Wang, S. L. *J. Solid State Chem.* **1989**, *80*, 127. (c) Phillips, M. L. F.; Harrison, W. T. A.; Gier, T. E.; Stucky, G. D.; Kulkarni, G. V.; Burdett, J. K. *Inorg. Chem.* **1990**, *29*, 2158. (d) Leclaire, A.; Chahboun, H.; Groult, D.; Raveau, B. *J. Solid State Chem.* **1986**, *65*, 168. (e) Huan, G.; Johnson, J. W.; Jacobson, A. J.; Corcoran, E. W.; Goshorn, D. P. *J. Solid State Chem.* **1991**, *93*, 514.

(6) Goodenough, J. B.; Hong, H. Y.-P.; Kafalas, J. A. *Mater. Res. Bull.* **1976**, *11*, 203.

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Table I. Chemical Analysis Data and Lattice Parameters of $Na_3V_2(PO_4)_3$, $Na_2V_2(PO_4)_3$, $V_2(PO_4)_3$ and Its Intercalation Products

compound	color	total vanadium, % found	total vanadium, % calcd	oxidation state of vanadium found	oxidation state of vanadium calcd	lattice parameters, Å *a*	lattice parameters, Å *c*
$Na_3V_2(PO_4)_3$	green	22.80	22.36	3.02	3.00	8.68 (2)	21.71 (2)
$Na_2V_2(PO_4)_3$	green	23.89	23.54	3.34	3.50	8.63 (2)	21.79 (2)
$V_2(PO_4)_3$	brown	26.21	26.34	4.56	4.50	8.52 (3)	22.02 (4)
$Li_{0.85}V_2(PO_4)_3$	yellowish-green	26.00	25.94	4.04	4.08	8.45 (4)	21.95 (5)
$Li_{2.40}V_2(PO_4)_3$	green	25.40	25.25	3.31	3.30	8.39 (2)	22.41 (4)
$Li_3V_2(PO_4)_3$	green	24.40	24.99	3.05	3.00	8.31 (2)	22.50 (2)
$H_3V_2(PO_4)_3$	greenish-black	26.35	26.14	3.04	3.00	8.57 (3)	22.48 (3)

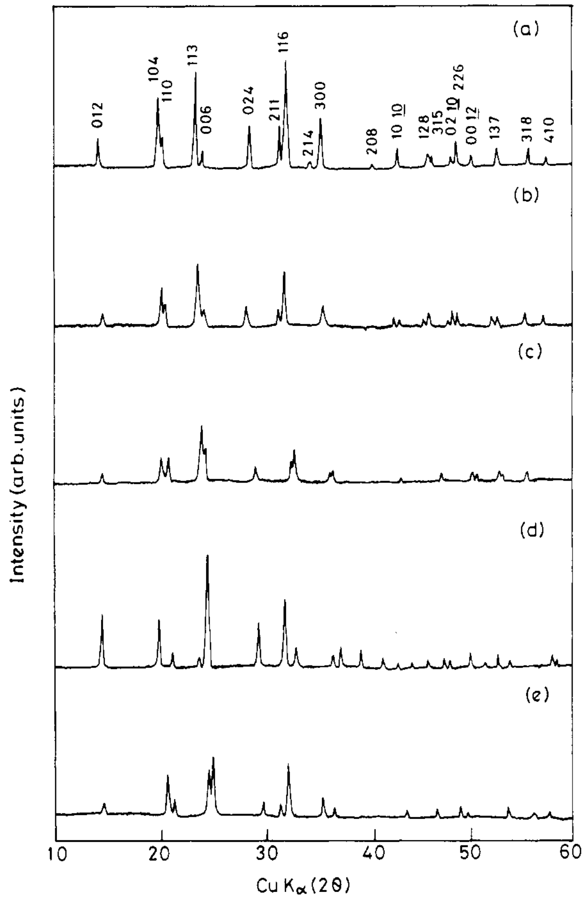

Figure 1. X-ray powder diffraction patterns of (a) $Na_3V_2(PO_4)_3$, (b) $Na_2V_2(PO_4)_3$, (c) $V_2(PO_4)_3$, (d) $Li_3V_2(PO_4)_3$, and (e) $H_3V_2(PO_4)_3$.

was 3.02 ± 0.02 as expected. We first tried to deintercalate sodium from $Na_3V_2(PO_4)_3$ using Br_2 in $CHCl_3$ as oxidizing agent since this reagent is known to deintercalate lithium from $LiVO_2$.[3e] We could readily remove one sodium forming $Na_2V_2(PO_4)_3$ by this method (Figure 1b and Table I). Prolonged reaction with Br_2 in $CHCl_3$ under reflux yielded a material close to the composition $NaV_2(PO_4)_3$, but the X-ray pattern showed indications of decomposition of the solid. Next, we employed Cl_2 in the same medium, in the deintercalation experiments. In a typical reaction, about 1 g of $Na_3V_2(PO_4)_3$ was suspended in 100 mL of $CHCl_3$ in an Erlenmeyer flask fitted with gas-passing provision. Chlorine gas was bubbled through the suspension (~10 mL/min) for about 12 h at room temperature. The suspension was stirred during the reaction. The solid after the reaction was recovered by filtration, washed with minimum quantity of CH_3CN, and vacuum dried. The oxidation state of vanadium in the solid as determined by redox titration was 4.56 ± 0.02, indicating that sodium had indeed been deintercalated completely from $Na_3V_2(PO_4)_3$, yielding $V_2(PO_4)_3$, the chemical reaction being

$$Na_3V^{III}_2(PO_4)_3 + {}^3\!/_2Cl_2 \rightarrow V^{IV}V^{V}(PO_4)_3 + 3NaCl$$

Table II. X-ray Powder Diffraction Data for $V_2(PO_4)_3$

h k l	d_{obs}, Å	d_{calc},[a] Å	I_{obs}
0 1 2	6.129	6.129	21
1 0 4	4.396	4.412	50
1 1 0	4.250	4.260	48
1 1 3	3.693	3.684	100
0 0 6	3.677	3.670	70
0 2 4	3.067	3.065	27
1 1 6	2.784	2.781	36
2 1 1	2.771	2.767	58
2 1 4	2.488	2.488	4
3 0 0	2.462	2.460	5
1 0 10	2.108	2.110	2
1 2 8	1.965	1.959	4
0 2 10	1.881	1.890	4
2 2 6	1.844	1.842	4
2 1 10	1.724	1.728	2
1 3 7	1.713	1.715	2
3 1 8	1.642	1.642	3

[a] Calculated for the lattice parameters given in Table I.

The X-ray powder diffraction pattern (Figure 1c and Table II) shows that $V_2(PO_4)_3$ possesses the same structure as the parent $Na_3V_2(PO_4)_3$, albeit with minor changes in the lattice parameters. The powder pattern of $V_2(PO_4)_3$ is indexable on a hexagonal cell with a = 8.52 (3) Å and c = 22.02 (4) Å, showing that the *a* axis contracts and the *c* axis expands on deintercalation (Tables I and II). It must be mentioned that while the isostructural $Nb_2(PO_4)_3$ has been prepared by a solid-state reaction,[7] we have not been able to prepare $V_2(PO_4)_3$ by a direct solid-state reaction route. Thus, low-temperature oxidative deintercalation of sodium from $Na_3V_2(PO_4)_3$ using Cl_2 in $CHCl_3$ has enabled us to synthesize the novel mixed-valent vanadium phosphate, $V_2(PO_4)_3$.

Since $V_2(PO_4)_3$ possesses the NASICON structure wherein the interstitial mobile cation sites are empty, we expected that it should be possible to insert chemically other electropositive atoms such as lithium and hydrogen. For lithium insertion, we treated about 1 g of $V_2(PO_4)_3$ with 100 mL of a 0.1 M solution of $LiI{\cdot}3H_2O$ in CH_3CN. There was instantaneous evolution of iodine on warming the solution to 50 °C, indicating insertion of lithium. After stirring the contents for 12 h, the solid was recovered, washed with CH_3CN, and dried. The oxidation state of vanadium in the product was 3.05 ± 0.02, and the powder X-ray diffraction was similar to the parent $V_2(PO_4)_3$ (Figure 1d and Table I), indicating that lithium had indeed been inserted giving the product, $Li_3V_2(PO_4)_3$. We could also prepare intermediate compositions $Li_{0.85}V_2(PO_4)_3$ and $Li_{2.4}V_2(PO_4)_3$ (Table I) by the same method showing that the solid solutions $Li_xV_2(PO_4)_3$ exist over a wide range of composition, most likely $0 \leqslant x \leqslant 3$.

We investigated the hydrogen insertion into $V_2(PO_4)_3$ by passing hydrogen gas at 200 °C for 18 h over $V_2(PO_4)_3$ dispersed with 1 wt % Pt. The oxidation state of vana-

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(7) Leclaire, A.; Borel, M. M.; Grandin, A.; Raveau, B. *Acta Crystallogr.* **1989**, *C45*, 699.

dium in the product was 3.04 ± 0.02, and the X-ray diffraction pattern was NASICON-like (Figure 1e), indicating that hydrogen insertion had indeed occurred.[8] The product could therefore be formulated as $H_3V_2(PO_4)_3$. We could not prepare $H_3V_2(PO_4)_3$ from $Na_3V_2(PO_4)_3$ by ion exchange because the latter dissolves in aqueous acids to give green solutions.

In summary, we have synthesized a new vanadium phosphate, $V_2(PO_4)_3$, that poossesses a NASICON-like structure, by oxidatively deintercalating sodium from $Na_3V_2(PO_4)_3$ using chlorine in $CHCl_3$ at room temperature. We have also shown that $V_2(PO_4)_3$ serves as a host material for reductive insertion of lithium and hydrogen under mild experimental conditions.

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[8] To find out whether hydrogen is inserted into or oxygen removed from $V_2(PO_4)_3$ during treatment with H_2 at 200 °C, we have recorded the IR spectrum of $H_3V_2(PO_4)_3$ and compared it with the spectra of $Na_3V_2(PO_4)_3$ and $V_2(PO_4)_3$. The spectra of all the compounds are similar (NASICON-like), showing characteristic absorption bands due to PO_4. If oxygen were removed during hydrogen treatment, the framework would have changed considerably, and this would have manifested in the IR spectrum. Moreover, it is known that in oxides such as WO_3 and $LaNiO_3$, hydrogen is inserted into the host rather than oxygen removed under similar experimental conditions.

Chemical Vapor Deposition of Thin Films of Ruthenium and Formation of an Unexpected Byproduct Using Hexafluoro-2-butynetetracarbonylruthenium(0)

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Metallic ruthenium exhibits several physical and chemical properties that make it interesting for applications in the electronics industry.[1] In addition to its metallic conductivity, it is both mechanically strong and chemically inert. Of further interest is the observation that ruthenium oxides (which form on the surface of ruthenium upon exposure to air) exhibit electrical conductivity similar to that of the metal.[2,3] This had led to some interest in using ruthenium as a contact material or diffusion barrier in devices.[4] Earlier work on the chemical vapor deposition of ruthenium utilized $Ru(acac)_3$,[4-6] $Ru_3(CO)_{12}$,[4] and (η^5-$C_5H_5)_2Ru$[4,7] to produce either ruthenium or ruthenium oxide films, depending on the carrier gas. The purest metallic films were prepared from $Ru_3(CO)_{12}$,[4] which has a relatively low vapor pressure. Unfortunately, the more volatile alternative, $Ru(CO)_5$, has a low stability which limits its use as a precursor.

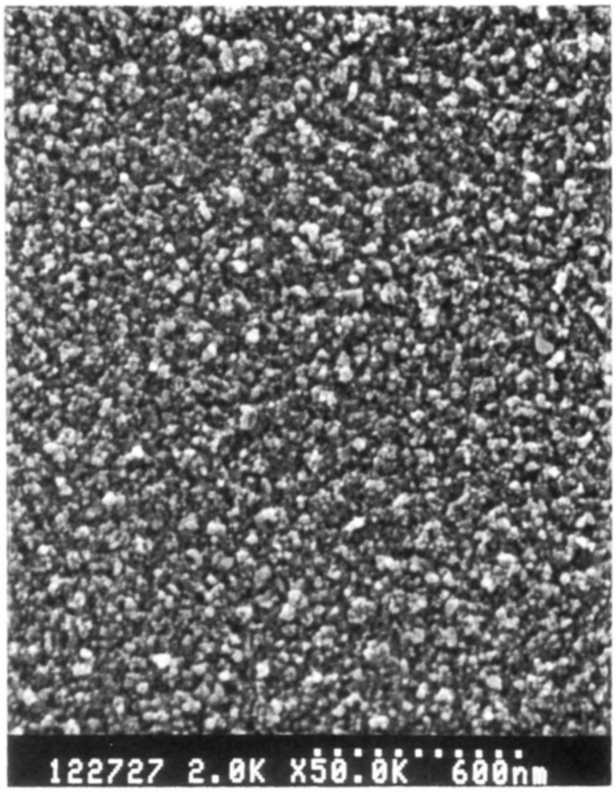
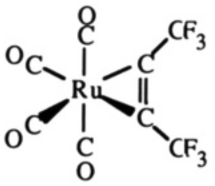


Figure 1. Scanning electron micrograph of a Ru film prepared at 500 °C using $Ru(hfb)(CO)_4$. The scale (600-nm total length) is located in the lower right-hand corner of the Figure.

Gagné and Takats recently reported[8] the synthesis of a series of monometallic alkyne carbonyl complexes of ruthenium, including $Ru(hfb)(CO)_4$, where hfb = hexafluoro-2-butyne, 1. Considering the often observed enhancement in volatility that fluorine substituents impart to compounds, we initiated a study of the CVD of ruthenium using $Ru(hfb)(CO)_4$. The compound was found to have a vapor pressure between 1 and 2 Torr at room temperature.



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The growth of Ru films was conducted without a carrier gas under a dynamic vacuum of approximately 1 mTorr in a hot-wall quartz reactor. The substrates, Si(100) wafers, were placed at several locations toward the entrance to the reactor. A profile of the furnace with the deposition tube present established that a reasonably constant temperature was achieved 2–3 cm from the beginning edge of the heating coils. The substrates were located at the beginning of the constant-temperature re-

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[1] Green, M. L.; Levy, R. A. *J. Met.* **1985**, *37* (6), 63.

[2] Vadimsky, R. G.; Frankenthal, R. P.; Thompson, D. E. *J. Electrochem. Soc.* **1979**, *126*, 2017.

[3] Rolison, D. R.; Kuo, K.; Umana, M.; Brundage, D.; Murray, R. W. *J. Electrochem. Soc.* **1979**, *126*, 407.

[4] Green, M. L.; Gross, M. E.; Papa, L. E.; Schnoes, K. J.; Brasen, D. *J. Electrochem. Soc.* **1985**, *132*, 2677.

[5] Viguié, J. C.; Spitz, J. *J. Electrochem. Soc.* **1975**, *122*, 585.

[6] Crosby, J. N.; Hanley, R. S. U.S. Patent 4,250,210, 1981.

[7] Trent, D. E.; Paris, B.; Krause, H. H. *Inorg. Chem.* **1964**, *3*, 1057.

[8] Gagné, M. R.; Takats, J. *Organometallics* **1988**, *7*, 561.

0897-4756/92/2804-0747$03.00/0