

Higher Valency Ion Substitution into the Manganese Oxide Framework

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Microporous materials give rise to a great deal of interest because of their uses for molecular sieving and catalysis.^{1,2} Manganese oxide octahedral molecular sieves (OMS) are a family of such compounds that form one-dimensional tunnel structures of various sizes.³ Because of mixed valent manganese, large open layers or tunnels, and high surface areas, these manganese oxide materials have been widely used in catalysis, separations, batteries, and chemical sensing.⁴ The potassium form of the mineral hollandite^{5a} is known as cryptomelane and has a chemical composition of $\text{KMn}_8\text{O}_{16}$.^{5b} This material is designated K-OMS-2 and possesses an average oxidation state of manganese of 3.9.

The crystal structure of cryptomelane is very porous, including one-dimensional tunnels among a rigid MnO_2 framework composed of edge-shared MnO_6 octahedra. The novel crystal structure and the mixed valence properties of manganese motivated us to investigate chemical alteration of the manganese oxide framework. Previous work has mostly concerned doping different divalent metal cations into the tunnels of OMS-2.^{5c,d} Very few studies have attempted the incorporation of lower valency cations into the framework of OMS-2.^{5e}

Here we report a new route for the synthesis of a novel nanocrystalline material with potential chemical sensing and catalytic applications by isomorphously substituting higher valency ion, namely, vanadium (V), into the manganese oxide matrix. The vanadium-substituted cryptomelane was synthesized hydrothermally at 200 °C for a period of 2 days by reacting manganese sulfate and sodium vanadate with potassium persulfate in the presence of potassium sulfate.

A typical synthesis of vanadium-substituted OMS-2 material, denoted K-V-OMS-2, involves the hydrothermal treatment of a 60-mL suspension composed of 14.3 mmol Mn, $\text{K}_2\text{S}_2\text{O}_8$, and K_2SO_4 in a molar ratio of 2:3:3. Sodium ortho-vanadate was added such that the Mn/V molar ratio varied from 4 to 19. The entire mixture was autoclaved at 200 °C for 2 days. The slurry formed was filtered, washed with deionized water, and dried at 120 °C overnight.

All vanadium derivatives give the same XRD pattern (Figure 1) equivalent to the vanadium-free OMS-2. There were no significant changes in the XRD peak intensities and line widths, and no additional peaks appeared, indicating that the vanadium centers are well-dispersed and that a segregated crystalline vanadia phase is absent. However, at higher vanadium loadings a decrease in peak intensities and an increase in the line broadening are observed. This indicates a decrease in the particle size and the presence of small structural distortions. Because of a minimal difference in size (1 pm) between Mn^{4+} and V^{5+} , the basal spacing of K-V-OMS-2 did not change with incorporation of increasing amounts of vanadium.

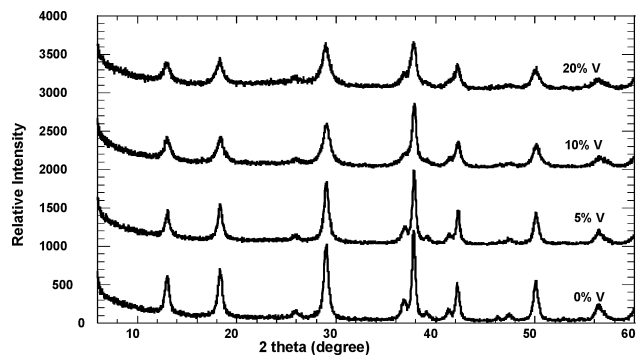


Figure 1. X-ray diffraction patterns for K-OMS-2 materials with different vanadium contents. Vanadium percentages are the ones present in the initial reaction mixture.

Table 1. Chemical Composition and Manganese AOS of K-OMS-2 and Vanadium Derivative Materials

initial %V	exptl. %V	EDX			AOS \pm 0.03
		%K	%V	%Mn	
0	0	8.5	0	91.5	3.87
5	4.8	8.6	4.4	87.0	3.62
10	8.1	7.9	7.5	84.6	3.34
20	11.0	7.9	10.1	82.0	3.09

To determine the exact vanadium content, elemental analyses via ICP and EDX were performed (Table 1). For the samples containing up to 10% V in the reaction mixture, there is a good correlation between the experimental vanadium percent determined by EDX or ICP and the initial vanadium content. However, the structure tends to favor a higher Mn/V ratio than the one initially present in the reaction mixture prior to crystallization, and the deviation from the initial composition increases with increasing vanadium concentration. EDX is used to analyze for K, V, and Mn and shows rising vanadium content correlated with a reduction in Mn percentage and a relatively constant K concentration, indicating that vanadium is isomorphously substituting for Mn in the framework rather than replacing K^+ ions in the tunnels.

Vanadium doping also caused a change in the average oxidation state (AOS)^{5e} of Mn (Table 1). The AOS for a vanadium-free cryptomelane is 3.9, confirming that both Mn^{3+} and Mn^{4+} are present in the structure, with Mn^{4+} being the predominant species.

The AOS of manganese gradually decreased with increasing vanadium content reaching the lowest value of 3.1. Because of similarity in size, V^{5+} is more likely to substitute for Mn^{4+} , resulting in more Mn^{3+} relative to Mn^{4+} in the V-doped cryptomelane framework. Since only a small decrease in K content is observed, we can conclude that Mn^{3+} is predominantly responsible for compensating the vanadium positive charge surplus, leaving the overall framework charge relatively unchanged.

The presence of out-of-framework vanadium compounds with structures possessing a Raman active $\text{V}=\text{O}$ bond (VO_2^{2+} , VO_2^+ ,

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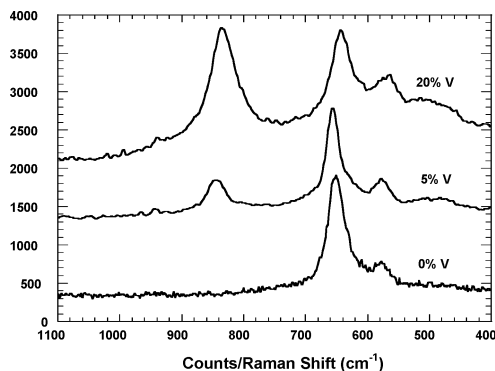


Figure 2. Raman spectra for V-free and V-substituted K-OMS-2. (The small features in the 650–800 and 950–1150 cm^{-1} range are caused by the angle of incidence of the laser beam on the sample surface.)

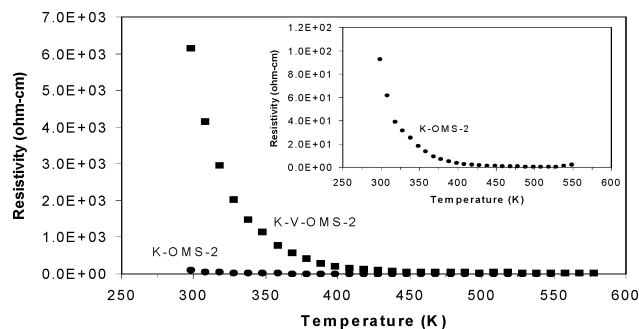


Figure 3. High-temperature resistivity of K-OMS-2 (inset) and K-V-OMS-2.

amorphous V_2O_5) was ruled out by employing Raman spectroscopy (Figure 2). The undoped K-OMS-2 spectrum exhibits two main peaks at 570 and 650 cm^{-1} characteristic of Mn-O lattice vibrations.^{6a} When vanadium is incorporated into the structure, only an additional peak at 830 cm^{-1} specific for V-O vibrations is observed.^{6b} The absence of the Raman active feature for the V=O bond in the 970–1030 cm^{-1} region suggests that no extra framework vanadium is present.

Electrical conductivity is a common property of the manganese mixed-valence compounds because of the partial filling of the Mn 3d orbital (electron hopping).⁷ DC resistivities were measured for the K-OMS-2 and vanadium derivatives at room temperature by the four-probe method, using a current of 0.1 mA. The resistivity values for K-OMS-2 and K-V-OMS-2 were 4.9×10^1 and $1.8 \times 10^3 \Omega \text{ cm}$, respectively.

Altering the Mn^{3+} – Mn^{4+} sequence by vanadium insertion creates traps for the electrons, which makes electron hopping difficult to occur, increasing the resistivity considerably. This trend was also observed at higher temperatures. Figure 3 shows the variable temperature data for K-OMS-2 and K-V-OMS-2 with the highest V content. Both samples exhibited an exponential variation of the resistivity with increasing temperature, previously observed for OMS-2⁷ and characteristic of a semiconductor material.⁸ The discrepancy in the resistivity values at room temperature between

the four-probe and two-probe methods is due to higher contact resistance inherent to the two-probe technique.

Electrical resistivity was also measured in the presence of humidity. K-V-OMS-2 material showed a decrease in resistivity of 31% upon changing from N_2 atmosphere to water-saturated N_2 at 27 $^\circ\text{C}$, while the variation in the resistivity for K-OMS-2 under the same conditions was negligible. The insertion of vanadium in the framework of OMS-2 may create vacancy sites in the manganese oxide structure, which could make possible the hopping of protons in the structure, enhancing the ionic properties of the material. This feature makes this material highly suitable for water sensing applications.

To generalize this approach for the insertion of the higher valency substituting ions into the manganese oxide framework, niobium was also successfully incorporated up to 5% into the K-OMS-2 structure via the same method using potassium niobate as niobium source.

In summary, microporous manganese oxide materials with novel chemical composition have been hydrothermally synthesized by incorporation of increasing amounts of higher valency cations into the manganese oxide framework. Vanadium and niobium were doped into the cryptomelane structure, lowering the manganese oxide average oxidation state and increasing its electrical resistivity. The OMS-2 syntheses set forth here represent a novel strategy for obtaining higher valency substituted microporous manganese oxides. Their further potential as catalysts and sensors is currently under investigation.

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