Sol−Gel Synthesis of Layered Birnessite-Type Manganese Oxides

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Layered birnessite-type manganese oxides have been synthesized by sol−gel reactions involving $KMnO_4$ or $NaMnO_4$ with glucose. These microporous manganese oxides are designated as *octahedral layer* materials, K-OL-1 and Na-OL-1, because their layered structure consists of edge-shared MnO_6 octahedra. The interlayer regions are occupied by alkali metal cations and water molecules. K-OL-1 and Na-OL-1 have been characterized by elemental analysis, powder X-ray diffraction, scanning electron microscopy, FT-IR spectroscopy, and Auger electron spectroscopy. The empirical formula of K-OL-1 has been determined to be $K_{0.28}MnO_{1.96}(H_2O)_{0.19}$. An interlayer spacing of 7 Å, typical of natural and synthetic birnessites, has been measured by X-ray diffraction. The sol−gel synthesis of K-OL-1 is carried out with concentrated aqueous solutions of glucose and $KMnO_4$ in a 1.5:1 mole ratio. Diluted reaction mixtures produce flocculent gels or precipitates which yield other manganese oxide phases such as cryptomelane and Mn_2O_3. The synthesis appears to be general for reactions of $KMnO_4$ with a variety of sugars as well as other polyalcohols such as ethylene glycol, glycerol, and poly(vinyl alcohol). Reactions between $NaMnO_4$ and glucose yield two related Na-OL-1 products. A procedure analogous to the K-OL-1 synthesis generates layered sodium birnessite materials with 5.5 and 7 Å interlayer distances. The 7 Å Na-OL-1 is obtained exclusively by hydrating the mixture of products. The 5.5 Å Na-OL-1 is prepared by calcining the Na-OL-1 xerogel at 800 °C instead of the typical 400 °C temperature. Both K-OL-1 and Na-OL-1 undergo significant yet incomplete cation extraction and ion exchange with monovalent and divalent cations.

Introduction

Birnessite is a common manganese oxide mineral found in soils, ore deposits, and marine manganese nodules.[1−5] The material has a two-dimensional layered structure that consists of edge-shared MnO_6 octahedra with cations and water molecules occupying the interlayer region,[5] Figure 1. The interlayer distance in birnessite is typically 7 Å, but further hydration can increase this spacing to produce a closely-related 10 Å birnessite known as buserite.[2−8] A dehydrated form of birnessite with a layer spacing of about 5.5−5.6 Å has also been identified.[8−11] Due to their octahedral layer (OL) structure, birnessite-type materials have been designated A-OL-1, in which A identifies the interlayer cation.[12] The OL-1 designation usually refers to 7 Å birnessite, but other layered manganese oxides can also be represented, for example, as 5.5 or 10 Å OL-1 materials.

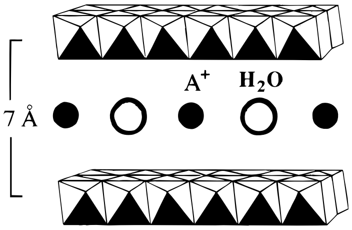

Figure 1. Illustration of the birnessite (A-OL-1) structure showing the layers of edge-shared MnO_6 octahedra with alkali metal cations (A^+) and water molecules in the interlayer region.

Despite their near-MnO_2 stoichiometry, birnessites are known to have variable and therefore poorly defined elemental compositions.[1,6] The birnessite formula is generally expressed as $A_xMn_{2\pm y}(H_2O)_z$, in which A typically represents an alkali metal cation. The average oxidation state of the mixed-valent manganese normally falls between 3.6 and 3.8, which represents a predominance of Mn(IV) with minor amounts of Mn(III).[2,6,13] There is also speculation over the presence of Mn(II).[2,6]

The interesting structural and physical properties of birnessite have prompted a variety of proposed applications for this material. The microporous nature of birnessite and its high relative abundance in marine manganese nodules make it an attractive candidate for heterogeneous catalysis. Indeed, birnessite may be responsible for the catalytic activity of crude manganese nodule samples, which are reported to promote a

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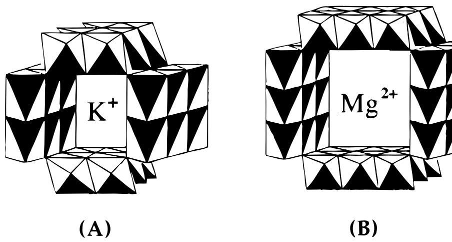

Figure 2. Illustrations of the hollandite and todorokite structures. (A) The hollandite structure with its 2 × 2 tunnel framework. This particular hollandite having K^+ in the tunnels is called cryptomelane. (B) The todorokite structure with its 3 × 3 tunnels. Todorokite having Mg^{2+} in the tunnel is the most common synthetic form of this material.

wide range of reactions that include oxidation of alcohols and CO, reduction of NO, hydrogenation of alkenes, and decomposition of organic sulfur compounds.[14−18] The microporosity and ion-exchange properties of birnessite have also been cited with regard to its potential use as an absorbent of heavy metal cations and noxious gases.[14] Layered metal oxides such as birnessite are also receiving considerable attention as cathode materials for rechargeable lithium batteries.[19−23]

Birnessites and other related OL-1 materials are also key synthetic precursors for manganese oxides with tunneled structures, such as hollandites and todorokites, Figure 2. Hollandite-type manganese oxides consist of approximately square tunnels with edge-shared MnO_6 octahedra in a 2 × 2 arrangement. The various hollandite members are distinguished only by the tunnel cation. Hollandite (Ba^{2+}) and cryptomelane (K^+, Figure 2A) are commonly synthesized by thermal[2,24−26] and hydrothermal[27] treatment of Ba-OL-1 and K-OL-1 precursors. Hydrothermal reactions of OL-1 materials have also been used to prepare less common hollandites such as manjiroite (Na^+) and coronadite (Pb^{2+}).[27] Todorokite has an analogous 3 × 3 tunnel structure with cations and water molecules occupying tunnel sites, Figure 2B. The synthesis of todorokite involves hydrothermal treatment of 10 Å OL-1 materials (buserites) that contain interlayer divalent cations such as Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}.[7,28−30] These 10 Å OL-1 precursors of todorokite are readily prepared by ion-exchange reactions with 7 Å Na-OL-1. The formation of tunneled manganese oxides from OL-1 precursors is believed to occur by a collapse of the layer framework around the interstitial cations. Depending on their size, these cations can serve as templates for different tunneled materials.[24,28−32] A survey of hydrothermal reactions involving several OL-1 compounds has revealed that a variety of manganese oxide products can be obtained, depending on the nature of the interlayer cation and the surrounding medium.[32] Synthetic routes to hollandite-type manganese oxides do not require OL-1 starting materials since a number of alternative procedures are known, especially in the case of cryptomelane.[25,33−35] However, todorokite has yet to be prepared without OL-1 precursors.

Synthetic OL-1 materials are commonly prepared by precipitation methods that involve oxidation of Mn^{2+} in concentrated aqueous base. A variety of oxidizing agents have been employed, such as O_2,[29,30,34,36−38] Cl_2,[34] $S_2O_8^{2-}$,[34] and MnO_4^-.[7] Several hydrothermal routes to OL-1 materials have also been reported. For example, slurries of MnO_2 and Mn_2O_3 in strong aqueous NaOH have been used to prepare Na-OL-1,[10,13,39] while K-OL-1 has been generated from MnO_2 in KOH solution[40] and from $KMnO_4$ in mild aqueous acid.[8] Various OL-1 materials with different interlayer cations can also be prepared by ion exchange. Sodium ions in birnessite are particularly labile, so Na-OL-1 is routinely used as a precursor for OL-1 derivatives with other monovalent and divalent cations.[2,13,28,36,38−42]

The sol−gel process is a less studied route to microporous manganese oxides yet offers a number of potential advantages over traditional synthetic procedures.[43−45] Sol−gel chemistry provides homogeneous mixing of reactants on the molecular level and can also be used to control shape, morphology, and particle size in the resulting products. The major obstacle in developing sol−gel processes for manganese oxides with near-MnO_2 stoichiometry is the lack of suitable Mn(IV) molecular precursors in aqueous solution.[46] An approach that circumvents this difficulty utilizes redox reactions between fumaric acid and aqueous permanganate solutions. This strategy has produced sol−gel syntheses of both birnessite[46,47] and cryptomelane.[48]

Here we describe the synthesis, characterization, and ion-exchange properties of birnessite-type manganese oxides prepared by sol−gel reactions between permanganate and glucose, as well as the extension of this procedure to other sugars and polyalcohols. The formation of manganese dioxide "jellies" was first reported by Witzrmann in 1915 from reactions of permanganate with sugars such as glucose, sucrose, galactose, fructose, and lactose.[49] These results were confirmed in subsequent studies,[50,51] but the gels remained uncharacterized until our

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reinvestigation of the work. A preliminary account of our research has been communicated.[12]

Experimental Section

Chemicals. Reagent grade chemicals were obtained commercially (Janssen, Fisher, or Aldrich) and used as received. Distilled deionized water was obtained from a Barnsted Nanopure II water-purifying system and used throughout.

Sol−Gel Synthesis of Potassium Birnessite (K-OL-1). A solution containing 3.0 g of $KMnO_4$ in 50 mL of water (0.38 M) was added quickly to a flask containing 5.0 g of glucose dissolved in 20 mL of water (1.4 M). The resulting mixture was swirled vigorously for 10−15 s and then allowed to stand without further agitation. The exothermic reaction produces a reddish sol which becomes a brown gel within 30 s of initial mixing. The gel was allowed to cool at room temperature for 30 min before being dried at 110 °C overnight. During the initial stages of drying, water was periodically decanted from the gel at 10−20 min intervals. Calcination of the resulting brown xerogel at 400 °C for 2 h produced an ash, which was ground into a fine brown/black powder. The powder was thoroughly washed four times with water and dried at 110 °C overnight. A typical isolated yield was 1.6 g.

Sol−Gel Synthesis of 7 Å Sodium Birnessite (7 Å Na-OL-1). A solution of 3.0 g of $NaMnO_4 \cdot H_2O$ in 50 mL of water (0.38 M) was added to a flask containing 5.0 g of glucose dissolved in 20 mL of water (1.4 M). The resulting mixture was swirled vigorously for 40−50 s and then allowed to stand without further agitation. The exothermic reaction produces a reddish sol which becomes a brown gel within 90 s of initial mixing. The gel was allowed to cool at room temperature for 30 min before being dried at 110 °C overnight. During the initial stages of drying, water was periodically decanted from the gel at 10−20 min intervals. Calcination of the resulting brown xerogel at 400 °C for 2 h produced an ash, which was ground into a fine brown/black powder. The crude product was stirred in water overnight before being isolated by filtration, washed twice with water, and dried at 110 °C. A typical isolated yield was 1.8 g.

Sol−Gel Synthesis of 5.5 Å Sodium Birnessite (5.5 Å Na-OL-1). A sodium birnessite xerogel was prepared as described above. The 5.5 Å sodium birnessite was obtained by calcining the xerogel at 800 °C for 2 h. The product was not washed with water to prevent partial conversion to the 7 Å sodium birnessite.

Cation Extraction and Ion Exchange. In a typical procedure, 0.5 g of birnessite was combined with 100 mL of a 1 M solution of the cation nitrate. The mixture was stirred for at least 24 h before the product was isolated by filtration, thoroughly washed four times with water, and dried at 110 °C.

Characterization. Powder X-ray diffraction (XRD) was performed with a Scintag 2000 PDS X-ray diffractometer using Cu Kα radiation. Samples were spread onto glass slides and scanned at 5° 2θ/min. The beam voltage and beam current settings were 45 kV and 40 mA, respectively. Electron microscopy was carried out using an AMRAY Model 1810 D scanning electron microscope and an acceleration potential of 30 kV. Diffuse reflectance IR spectra were obtained using a Nicolet SX-60 FT-IR spectrometer. Auger electron spectra were obtained with a Perkin-Elmer PHI 610 scanning Auger microprobe. Elemental analysis for metals was carried out by flame atomic absorption spectroscopy using a Perkin-Elmer Model 2380 AA instrument. The elemental analysis for carbon was performed by Galbraith Laboratories. Average oxidation states for manganese were determined by iodometric titration.[52]

Results and Discussion

Potassium Birnessite (K-OL-1). The sol−gel synthesis of potassium birnessite (K-OL-1) is shown schematically in Figure 3. The rapid and exothermic reaction between $KMnO_4$ and glucose produces a brown gel which, upon drying and calcination, yields crude K-OL-1 as a brown/black powder. Purified K-OL-1 is obtained after washing with distilled deionized water. Unlike traditional sol−gel processes that produce gels from hydrolyzed metal alkoxides, the reaction between $KMnO_4$ and glucose promotes gelation through the reduction of MnO_4^-. The gel matrix is likely to consist of manganese oxide sites that are cross-linked by a network of partially oxidized glucose fragments, Figure 4. The formation of "manganese dioxide jellies" from reactions between $KMnO_4$ and sugars was originally reported over 80 years ago.[49] However, these gels were poorly characterized and not subjected to drying and calcination until our follow-up work.[12] Birnessite also has been prepared by a similar sol−gel reaction between concentrated permanganate and fumaric acid.[46]

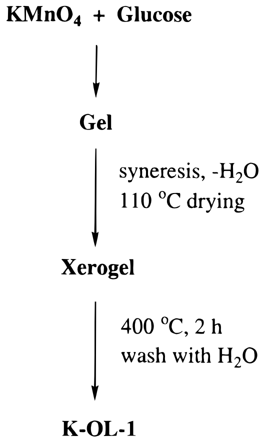

Figure 3. Schematic diagram showing the sol−gel synthesis of K-OL-1.

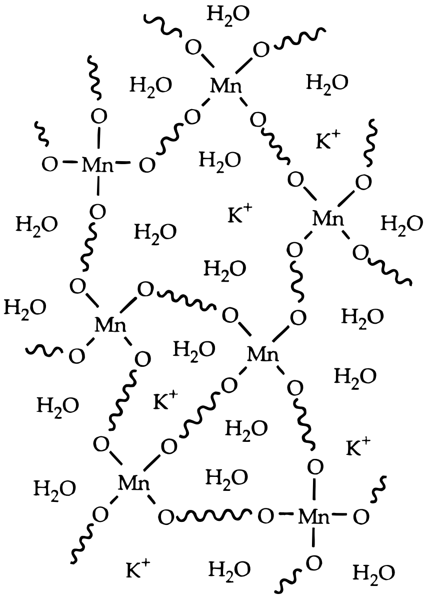

Figure 4. Illustration of the cross-linking proposed for manganese oxide gels.

The powder X-ray diffraction pattern of sol−gel K-OL-1 is shown in Figure 5. The pattern is dominated by two major peaks at 7.0 Å (002) and 3.5 Å (212), which are signature features of synthetic birnessite materials. Similar XRD patterns are also observed for natural birnessites from marine manganese concretions. However, peaks from mineral samples are considerably broader compared to the peaks from sol−gel K-OL-1, indicating lower crystallinity.[42] The peak at 7 Å is particularly significant, as it represents the Mn−Mn distance from adjacent layers. A survey of the many reports of synthetic birnessites suggests that the position of this peak can vary by a few tenths of an angstrom. The layered structure of birnessite

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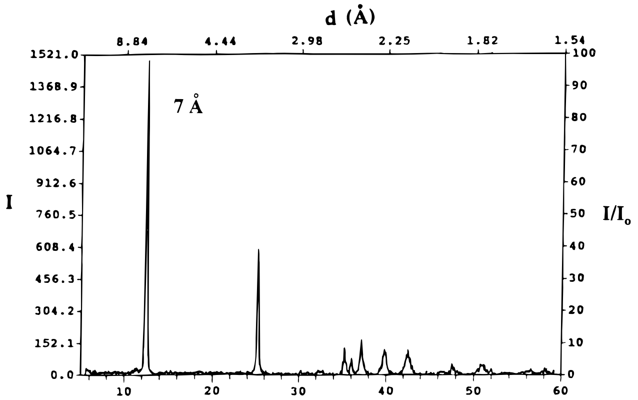

Figure 5. Powder XRD pattern of sol−gel K-OL-1.

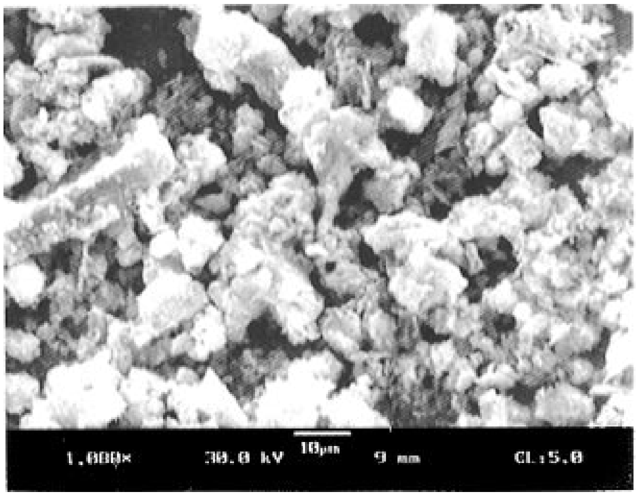

Figure 6. SEM photograph of sol−gel K-OL-1.

was originally modeled after that of chalcophanite, $ZnMn_3O_7(H_2O)_3$, which has a similar XRD pattern and shows an analogous crystal morphology according to TEM.[53] The octahedral layers of chalcophanite have vacancies in one-seventh of the Mn sites, with interlayer zinc cations residing above and below these vacancies and positioned between the manganese oxide layer and a sheet of interlayer water molecules.[5,54] Structure determinations from powder XRD refinements on synthetic sodium and potassium birnessites reveal a similar layered structure, but with few Mn vacancies and only one interlayer plane containing both the cations and water molecules,[5] as shown in Figure 1. Scanning electron microscopy (SEM) of sol−gel K-OL-1 reveals a nondescriptive particle morphology, Figure 6, which agrees with SEM photographs of non-sol−gel potassium birnessites.[34]

An empirical formula of $K_{0.28}MnO_{1.96}(H_2O)_{0.19}$ was determined for sol−gel K-OL-1 from elemental composition and manganese oxidation state data. Percentages of potassium (10.9%) and manganese (54.9%) were obtained from atomic absorption spectroscopy, while the oxygen content (34.2%) was found by difference after assuming negligible hydrogen from interlayer water. The carbon content was analyzed at less than 0.5%. Iodometric titration was used to determine an average manganese oxidation state of 3.63, which is important in determining how the oxygen content is divided between the oxide layers and interlayer water. Compared with those of other layered manganese oxides, the potassium percentages and manganese oxidation states in sol−gel K-OL-1 have normal values. However, the water content (H_2O:Mn ratio 0.19) is significantly lower than those of non-sol−gel materials (H_2O:Mn ratio 0.3−1.0).[6,40] Sol−gel K-OL-1 is therefore less readily hydrated and possesses interlayer vacancies that normally contain water. The amount of water from the empirical formula translates to 3.4% by weight, which agrees adequately with thermogravimetric analysis showing 5% weight loss due to water (as detected by FT-IR) between 75 and 175 °C.

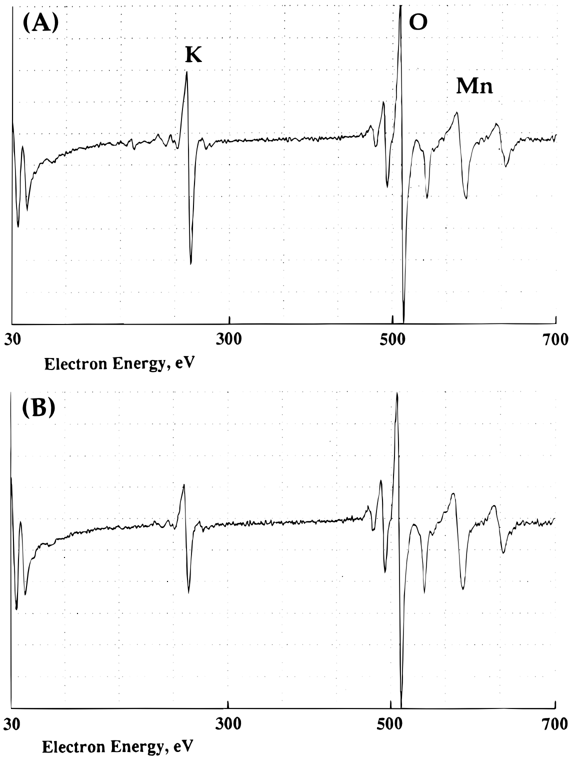

Figure 7. Auger electron spectra of sol−gel K-OL-1: (A) before washing with water; (B) after washing. The units of the vertical axis are d*N*(*E*)/d*E*. The peaks represent potassium (LMM: 252 eV), oxygen (KLL: 503 eV), and manganese (LMM: 542, 589, and 635 eV).

Crude K-OL-1 obtained after calcination but before washing contains considerable amounts of surface-adsorbed potassium ions. Elemental analysis of an unwashed sample typically gives potassium percentage that is twice the post-washing value. An Auger analysis of K-OL-1 supports the claim that excess potassium is adsorbed on the surface, Figure 7. The potassium LMM signal at 252 eV decreases by about half after washing with water, whereas the Auger signals for oxygen and manganese are unchanged.

The diffuse reflectance IR spectrum of sol−gel K-OL-1 is shown in Figure 8. The strong, broad absorbance at 3290 cm^{-1} is attributed to the O−H stretch of interlayer water molecules and framework hydroxyl groups. The apparent absence of a distinct deformation band for water near 1600 cm^{-1} suggests that this absorbance is weak and broad as a result of poor interlayer hydration. Such an interpretation is consistent with the low water content determined from elemental analysis and TGA experiments. In addition, an IR study of natural and synthetic manganese oxides shows the intensity of this peak varying among different birnessite samples.[55] The possibility of framework hydroxyl groups in sol−gel K-OL-1 is also consistent with the IR spectrum, since hydroxyl moieties contribute to O−H stretching but not to water deformation. The hydroxyl groups can occupy interlayer vacancies that are created

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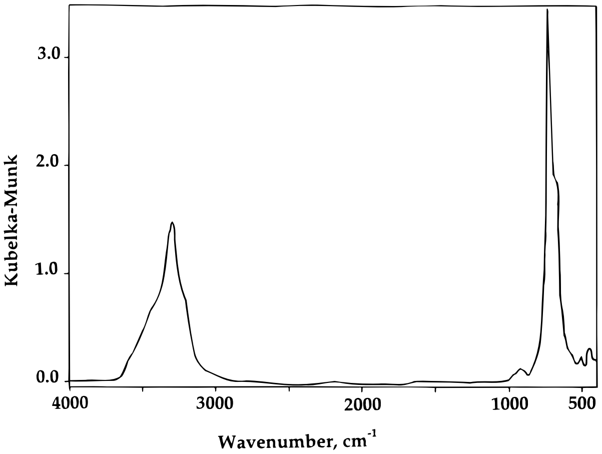

Figure 8. Diffuse reflectance IR spectrum of sol−gel K-OL-1.

Table 1. Reactions of $KMnO_4$ and Glucose with Different Relative Concentrations ($[KMnO_4]$ = 0.27 M)

[glucose] (M)	glucose:$KMnO_4$	initial phase	final product
0.40	1.5	gel	birnessite
0.20	0.74	gel	birnessite
0.10	0.37	flocculent gel	cryptomelane
0.05	0.2	flocculent gel	amorphous MnO_x

by the deficiency of water molecules in sol−gel K-OL-1. The other prominent feature of the IR spectrum is a peak at 720 cm^{-1}, which is believed to be associated with the manganese oxide lattice. The location of this peak is at a high frequency compared to the 650−400 cm^{-1} range typically observed for birnessites.[55] This apparent peak shift has not been reconciled.

The sol−gel process for K-OL-1 is very sensitive to variations in reaction conditions. The synthesis proceeds smoothly in mildly basic solutions of $KMnO_4$ and glucose without additional acid or base. An increase in basicity accelerates gelation but does not improve the quality of the K-OL-1 product. By contrast, acidified reaction mixtures promote considerable decomposition to soluble Mn^{2+} and solid Mn_2O_3 (bixbyite).

Results from sol−gel reactions between $KMnO_4$ and glucose with different *relative* concentrations are presented in Table 1. In these experiments, a $KMnO_4$ concentration of 0.27 M was used while the concentration of glucose was varied between 0.40 and 0.05 M, giving glucose:$KMnO_4$ ratios of 1.5−0.2. The formation of monolithic gels that yield K-OL-1 is favored by high reactant concentrations (0.27 M $KMnO_4$, 0.2−0.4 M glucose) and large relative amounts of glucose (glucose:$KMnO_4$ ratio 1.5). By contrast, when the glucose concentration is lowered to 0.10 M, decreasing the glucose:$KMnO_4$ ratio to 0.37, a flocculent gel is produced and the tunneled manganese oxide, cryptomelane (Figure 2A), is obtained after drying and calcination. Further lowering of the glucose:$KMnO_4$ ratio to 0.2 also results in a flocculent gel, but the calcined product becomes an amorphous manganese oxide. The sol−gel pathway that leads to cryptomelane instead of birnessite can be rationalized from the lower relative glucose concentration and concurrent fragmentation of the resulting gel. Dilute glucose solutions contain fewer cross-linking molecules to interconnect the manganese oxide centers. As a consequence, the gel matrix weakens and becomes flocculent. The fragmentation exposes more surface area on the gel and enhances the ability of the surrounding medium to extract K^+. Gels with lower K^+ concentrations are more likely to form cryptomelane because of its significantly lower potassium content (K:Mn = 0.125 and % K = 5.3, based on KMn_8O_{16})[25] compared to sol−gel birnessite (K:Mn = 0.28 and % K = 10.9). Dilute glucose solutions are also expected to be less effective in reducing permanganate, which also favors cryptomelane with its slightly higher manganese valence (3.88) compared to that of sol−gel birnessite (3.63). A related birnessite system, prepared from $KMnO_4$ and fumaric acid, is also observed to undergo a conversion from birnessite to cryptomelane when the fumaric acid:$KMnO_4$ ratio is lowered from 1:3 to 1:4.[56] However, in this case the solution acidity is also increased, thereby changing the nature of the reaction from sol−gel type to precipitation type.

Table 2. Reactions of $KMnO_4$ and Glucose with Different Overall Concentrations[a]

$[KMnO_4]$	[glucose] (M)	dilution factor	initial phase	final product
0.16	0.23	1.0	gel	birnessite
0.06	0.09	0.4	flocculent gel	cryptomelane/Mn_2O_3
0.03	0.05	0.2	precipitate	Mn_2O_3

[a] Glucose:$KMnO_4$ = 1.5:1.

Results of sol−gel reactions with different *overall* concentrations of $KMnO_4$ and glucose are summarized in Table 2. High overall concentrations favor the formation of monolithic gels that serve as precursors to birnessite. Lesser overall concentrations produce flocculent gels that give mixtures of cryptomelane and Mn_2O_3. At very low concentrations, precipitates that exclusively yield Mn_2O_3 are generated. Fragmentation of the gel at lower overall concentrations is not surprising, given the lower cross-linking density upon gelation. As discussed previously for relative reactant concentrations, the preferential formation of different manganese oxide products is apparently related to retention of K^+ in the gel. Greater fragmentation promotes extraction of K^+, which in turn favors the formation of manganese oxide products having less potassium.

The sol−gel synthesis of K-OL-1 has been extended to other sugars and different polyalcohols. The procedures are essentially the same as the one used for $KMnO_4$ and glucose. Reactions of $KMnO_4$ with sucrose, fructose, and galactose produce gels that ultimately yield birnessite after drying and calcination. Similarly, concentrated aqueous solutions of polyalcohols such as ethylene glycol, glycerol, and poly(vinyl alcohol) can also be used to prepare sol−gel K-OL-1. Gels and K-OL-1 are also generated from reactions between allyl alcohol and $KMnO_4$, indicating that olefin groups can also be employed in this process. The birnessite products from these reactions were all characterized by X-ray diffraction. Monofunctional alcohols such as ethanol and 2-propanol also react with $KMnO_4$, but these processes generate precipitates rather than gels, even with highly concentrated mixtures. Calcination of the precipitates yields cryptomelane according to XRD analysis. The formation of precipitates undoubtedly reflects the inability of the monofunctional alcohols to serve as cross-linking agents. Interestingly, however, precipitates generating cryptomelane are also obtained with 1,4-butanediol, which suggests that the gelation mechanism requires a minimum density of functional groups on the polyalcohol. The results of these experiments agree with the above observations that monolithic gels are typically precursors to birnessite, whereas flocculent gels and precipitates favor cryptomelane and other manganese oxide products.

Sol−gel K-OL-1 is stable under aqueous refluxing conditions and can withstand hydrothermal treatment up to 160 °C. The material transforms into cryptomelane when heated dry at 600 °C for 24 h, consistent with similar experiments on potassium birnessites prepared by non-sol−gel methods.[2,25,26] Heat treatment at 800 °C for 24 h initiates degradation to Mn_3O_4

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(56) Bach, S.; Pereira-Ramos, J. P.; Baffier, N. *Solid State Ionics* **1995**, *80*, 151.

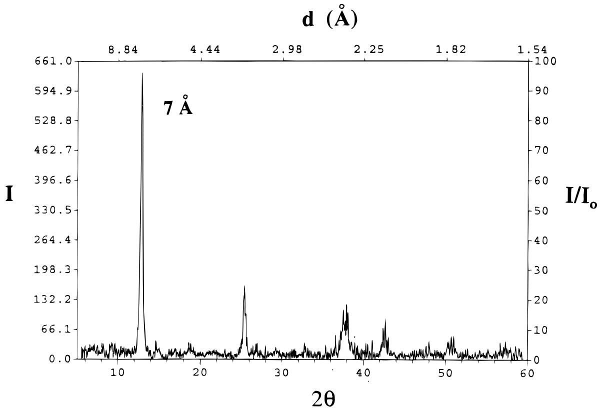

Figure 9. Powder XRD pattern of 7 Å sol−gel Na-OL-1.

(hausmannite), although significant amounts of K-OL-1 are still present according to XRD analysis. Heating at 1000 °C for 24 h results in total degradation to Mn_3O_4. These results are again consistent with previous work.[2,25,26]

Sodium Birnessite (Na-OL-1). The sol−gel synthesis of sodium birnessite is complicated by the observation of two related Na-OL-1 materials, both of which are generated from $NaMnO_4$ and glucose using the identical procedure followed for K-OL-1. Both materials have layered structures, but XRD analysis detects one with an interlayer distance of 7 Å, analogous to that of K-OL-1, and another with a layer spacing of 5.5 Å. Prolonged stirring of this product mixture in water converts the 5.5 Å Na-OL-1 into the 7 Å form. The XRD pattern of the 7 Å Na-OL-1 is characteristic of a birnessite-type species that is very similar to K-OL-1, Figure 9. The SEM analysis of 7 Å Na-OL-1 also reveals the same particle morphology observed for K-OL-1. This appearance is quite different compared to that of non-sol−gel sodium birnessites, which typically form as platelets.[30] An empirical formula of $Na_{0.33}MnO_{2.04}(H_2O)_{0.25}$ has been determined for 7 Å Na-OL-1 based on the elemental composition of Na (7.7%) and Mn (55.4%) and an average manganese oxidation state of 3.76.

The sol−gel synthesis of Na-OL-1 differs from the K-OL-1 procedure in its insensitivity to variations in reactant concentration. Changes in both the relative and overall concentrations of glucose and $NaMnO_4$ lead to fragmented gels, yet Na-OL-1 is consistently the only manganese oxide product of this reaction. By contrast, the sol−gel reactions discussed previously for K-OL-1 could be diverted to other manganese oxides such as cryptomelane (K-hollandite) and Mn_2O_3 by lowering the reactant concentrations. In the Na-OL-1 scheme, the absence of a competing process for manjiroite (Na-hollandite) is probably due to the relative stabilities of Na-OL-1 and manjiroite compared to K-OL-1 and cryptomelane. Structural studies on cryptomelane have concluded that K^+ fits almost ideally in the 4.6 Å hollandite tunnel framework.[57,58] A similar conclusion was drawn from cation extraction/insertion experiments on hollandites with different alkali metal cations.[35] The size of the K^+ cation therefore makes it an excellent template for the hollandite structure and likely accounts for the many synthetic routes to cryptomelane. By contrast, the smaller Na^+ cation is an inferior template for the hollandite structure, so the sol−gel reactions between permanganate and glucose are less likely to yield manjiroite.

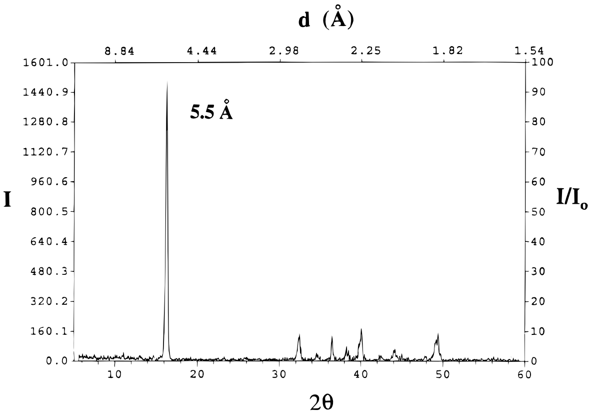

Figure 10. Powder XRD pattern of 5.5 Å sol−gel Na-OL-1.

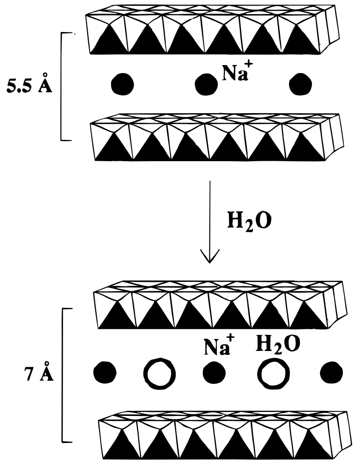

Figure 11. Relationship between the 5.5 Å (dehydrated) and 7 Å (hydrated) forms of Na-OL-1.

Unlike K-OL-1, which transforms into cryptomelane at 600 °C and then decomposes to Mn_3O_4 above 800 °C, sol−gel 7 Å Na-OL-1 converts directly to Mn_3O_4 upon heating at 600 °C for 2 h. This result again points to the relative effectiveness of K^+ over Na^+ in stabilizing the hollandite structure. Sol−gel Na-OL-1 is indefinitely stable at 150 °C under hydrothermal conditions. By contrast, non-sol−gel Na-OL-1 materials yield manganite, Mn(O)OH, when treated hydrothermally at 150 °C for 24 h.

The 5.5 Å Na-OL-1 is obtained by calcining Na-OL-1 xerogels at 800 °C instead of the usual 400 °C temperature. Washing with water causes partial conversion to 7 Å Na-OL-1. The isolation of 5.5 Å Na-OL-1 has been verified by XRD, Figure 10. Layered manganese oxides with *d* spacings near 5.5 Å were previously observed and characterized as dehydrated forms of 7 Å sodium birnessite,[8−11] Figure 11. In the structure of these 5.5 Å materials, Na^+ appears to be nestled within a trigonal prismatic array of oxygen atoms from adjacent manganese oxide layers.[59,60] The accommodation of Na^+ (ca. 1.0 Å ionic radius) within a cavity formed by adjacent layers (thickness ca. 4.4 Å[61]) allows some degree of overlap between the Na^+ cation sphere and the manganese oxide layers along the axis perpendicular to the layer framework. This configuration seems to account for the fact that direct stacking of Na^+ and the layers requires an interlayer distance of 6.4 Å, which is larger than the observed 5.5 Å spacing.

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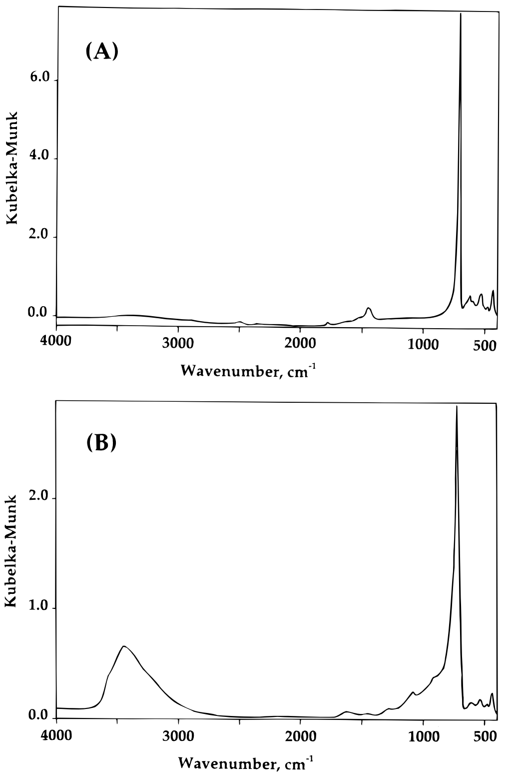

Figure 12. Diffuse reflectance IR spectra of sol−gel Na-OL-1 materials showing differences in absorbance due to interlayer hydration: (A) 5.5 Å Na-OL-1; (B) 7 Å Na-OL-1.

The identification of 5.5 Å Na-OL-1 as a dehydrated birnessite has been confirmed by the complete conversion of this material into 7 Å Na-OL-1 after prolonged stirring in water. Exposure to humidity also promotes this transformation, but at a much slower rate. Infrared absorbance bands for interlayer water are absent in the diffuse reflectance IR spectrum of 5.5 Å Na-OL-1, Figure 12A. By contrast, an O−H stretching band at 3450 cm^{-1} is readily apparent in the spectrum of 7 Å Na-OL-1, along with a weak, broad band for H_2O deformation just above 1600 cm^{-1}, Figure 12B. A reliable elemental analysis of 5.5 Å Na-OL-1 has not been obtained, since surface-adsorbed Na^+ could not be washed from the crude product without introducing some 7 Å Na-OL-1. Attempts to purify the material by washing with nonaqueous solvents such as methanol, acetonitrile, and DMSO were unsuccessful.

Higher calcination temperatures clearly favor the conversion of xerogels into 5.5 Å Na-OL-1. Xerogels heated at 400 °C produce mixtures containing both 5.5 and 7 Å Na-OL-1 in significant proportions, whereas calcination at 600 °C yields 5.5 Å Na-OL-1 with only minor amounts of the 7 Å material. At 800 °C, 5.5 Å Na-OL-1 is the exclusive manganese oxide product. Although 5.5 Å Na-OL-1 is a dehydrated form of 7 Å Na-OL-1, there is no evidence to suggest that the 7 Å material serves as a precursor to 5.5 Å Na-OL-1 during calcination. Indeed, it was noted earlier that 7 Å Na-OL-1 degrades to Mn_3O_4 at temperatures above 600 °C. Attempts to convert 7 Å Na-OL-1 into the 5.5 Å form using a reported treatment with aqueous NaOH[10] were unsuccessful.

The high thermal stability of 5.5 Å Na-OL-1 relative to 7 Å Na-OL-1 might be a function of interlayer hydration. The loss of water in these materials is an important phenomenon which may be responsible for structural modifications that initiate a collapse of the 7 Å layers. By comparison, the dry and compressed layers of 5.5 Å Na-OL-1 are not susceptible to this type of low-temperature structural change, thus its greater thermal stability.

Table 3. Cation-Extraction/Ion-Exchange Results for K-OL-1 and Na-OL-1[a]

K-OL-1			Na-OL-1		
cation	% K	deg of exchange	cation	% Na	deg of exchange
K^+	10.9	1.00	Na^+	7.7	1.00
H^+	2.4	0.22	H^+	0.7	0.09
NH_4^+	0.5	0.05	NH_4^+	0.7	0.09
Li^+	1.6	0.15	Li^+	1.6	0.21
Na^+	2.5 (% Na: 5.5)	0.23	K^+	0.7 (% K: 6.7)	0.09
Mg^{2+}	3.9 (% Mg: 3.7)	0.36	Mg^{2+}	2.5 (% Mg: 2.9)	0.33
Cu^{2+}	2.5 (% Cu: 7.0)	0.23	Cu^{2+}	2.8 (% Cu: 6.9)	0.36

[a] Cation extraction is based on depletion of K^+ and Na^+. The exchange cation was analyzed for selected elements, as indicated by percentages in parentheses.

Alkali Metal Extraction from Sol−Gel Birnessites. Cation extractions of sol−gel K-OL-1 and Na-OL-1 were carried out in stirred 1 M solutions of a foreign cation for 24 h at ambient temperature. Longer stirring times and higher temperatures did not improve the extraction process as judged by the loss of alkali metal. The extractions of interlayer cations and insertions of selected foreign cations are comparable for both K-OL-1 and Na-OL-1, Table 3. However, complete extraction of K^+ or Na^+ was not achieved. This is unusual for Na-OL-1, since non-sol−gel sodium birnessites typically have labile sodium cations that undergo essentially 100% replacement in ion-exchange reactions.[36,60] In general, sol−gel K-OL-1 and Na-OL-1 have poorly labile interlayer cations compared to their non-sol−gel counterparts.

The extraction of alkali metal cations from microporous manganese oxides has been shown to occur by two possible mechanisms, a simple ion-exchange-type process and a redox-type reaction.[13,35,62] In this study, the two mechanisms were not differentiated and cation extraction was treated as an ion-exchange process. Reports of alkali cation extraction by acid treatment of microporous manganese oxides suggest that this is the favored pathway. For example, the ion-exchange mechanism accounts for about 80% of the Na^+ extraction resulting from acid treatment of non-sol−gel sodium birnessite.[13]

Attempts to convert Na-OL-1 and K-OL-1 from 7 Å birnessites to 10 Å buserites by ion exchange were unsuccessful. In non-sol−gel sodium birnessites, a virtually complete exchange of Na^+ with various divalent cations leads to the formation of buserites, [28−30,36,38,60] which are similar to birnessites but have 10 Å *d* spacings due to an additional layer of interstitial water. However, reactions of sol−gel OL-1 materials with divalent cations such as Mg^{2+} and Cu^{2+} result in partial ion exchange with retention of the 7 Å interlayer distance. Buserites are of interest because they are key precursors in the synthesis of todorokites, a class of tunneled manganese oxides, Figure 2. There are few documented procedures for synthesizing todorokites, and all involve hydrothermal alteration of 10 Å buserites.[7,28−31] By contrast, there are numerous methods of preparing other microporous manganese oxides, such as birnessites and hollandites.

The incomplete ion-exchange reactions involving sol−gel Na-OL-1 and K-OL-1 have not been fully rationalized. It is also not obvious why these materials resist hydration beyond the 7 Å form. The unexceptional levels of Na^+ and K^+ make it unlikely that interlayer charge density plays much of a role in stabilizing the 7 Å layers against expansion to 10 Å. Indeed, the conversion of 5.5 Å Na-OL-1 to 7 Å Na-OL-1 clearly

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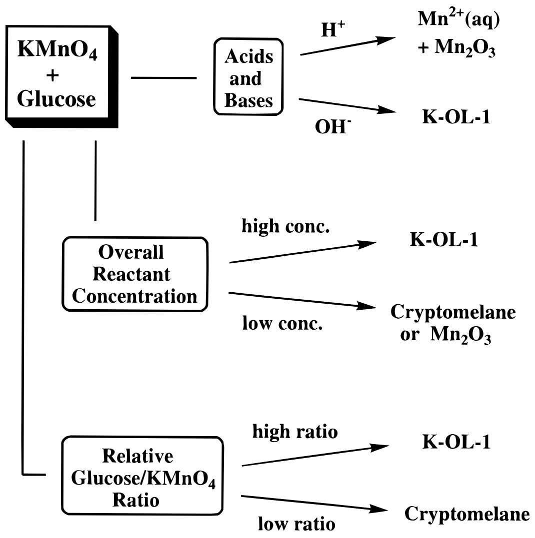
(62) Feng, Q.; Kanoh, H.; Miyai, Y.; Ooi, K. *Chem. Mater.* **1995**, *7*, 1722.

Scheme 1

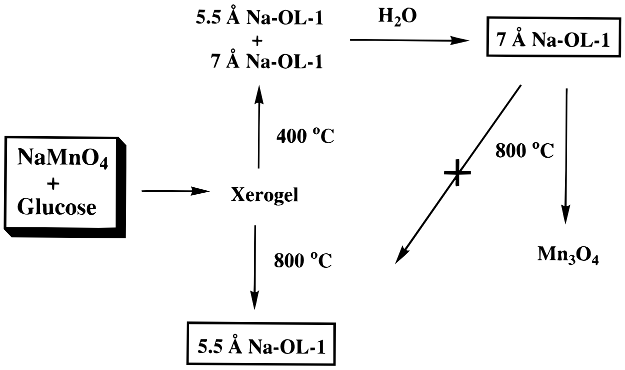


indicates that layer expansion is possible in these sol−gel systems. A key factor may be the unusually low interlayer water content, which might limit cation mobility between the 7 Å layers and restrict access to all the ion-exchange sites. Such a scenario would particularly affect the most strongly hydrated metal cations and tend to suppress further hydration between the birnessite layers. Since 10 Å buserites have significantly larger amounts of interlayer water compared to 7 Å birnessites, the incomplete ion exchange only serves to exacerbate the difficulty of layer expansion in the already poorly-hydrated sol−gel K-OL-1 and Na-OL-1 materials.

Conclusions

The layered birnessites, K-OL-1 and Na-OL-1, have been prepared by sol−gel redox reactions between permanganate and glucose. The procedure appears to be general for different sugars as well as for a variety of other polyalcohols. Reactions between $KMnO_4$ and glucose are strongly dependent on solution conditions and concentration, as summarized in Scheme 1. By contrast, the chemistry of $NaMnO_4$ and glucose is less dependent on reaction conditions.

Scheme 2



The sol−gel synthesis of Na-OL-1 initially produces two related materials, one with a 5.5 Å interlayer distance and another with a 7 Å spacing. The 5.5 Å Na-OL-1 has been identified as a dehydrated layered material which can be converted to 7 Å Na-OL-1 upon hydration. The reverse process, conversion of 7 Å Na-OL-1 into 5.5 Å Na-OL-1, has not been accomplished. Chemistry of the sol−gel Na-OL-1 system is summarized in Scheme 2.

The interlayer cations of K-OL-1 and Na-OL-1 undergo partial extraction and ion exchange with foreign cations. However, there is yet no evidence for the conversion of sol−gel birnessites into 10 Å buserites. The inability of these OL-1 materials to form buserites may be related to their unusually low concentrations of interlayer water.

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