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Sol−Gel Synthesis of Birnessite from $KMnO_4$ and Simple Sugars

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Birnessite is a naturally occurring manganese oxide that has been identified as a major constituent of deep sea manganese nodules.[1] The mineral consists of layers of edge- and corner-linked MnO_6 octahedra with water molecules and alkali-metal cations in the interlayer voids (Figure 1). A generalized elemental composition of birnessite is $A_xMnO_{2\pm y}{\cdot}zH_2O$, in which A represents an alkali-metal cation.[2] Natural and synthetic birnessites with an octahedral layered (OL) structure have attracted significant interest because of their potential as heterogeneous catalysts[3,4] and materials for secondary batteries.[5−7] Birnessites are also precursors for tunnel structure manganese oxides such as cryptomelane[8,9] and todorokite.[10,11] Sol−gel processing of birnessites potentially offers numerous advantages over traditional methods of synthesis such as high-purity, particle-size homogeneity, and film-casting capability.[12,13] However, very few sol−gel routes have been developed for materials with near-MnO_2 stoichiometry such as birnessite.[5−7,14,15] Early reports of manganese oxide gels described "MnO_2 jellies" formed from reactions of $KMnO_4$ with simple sugars.[16−18] However, until now these systems remained poorly characterized. We have reinvestigated these manganese oxide gels and in the process discovered a new sol−gel method of preparing birnessite with interlayer potassium cations, K-OL-1.

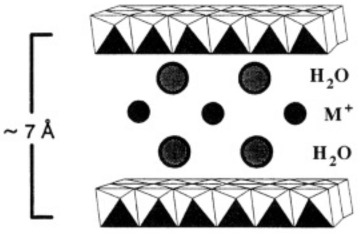
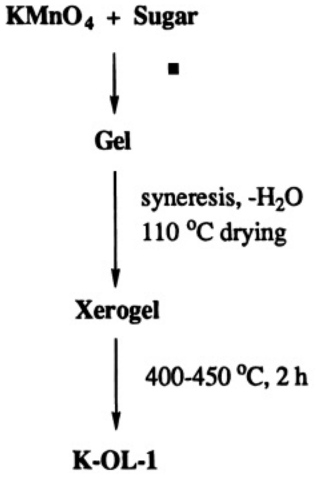


Figure 1. Structural diagram of birnessite showing layers of edge- and corner-sharing MnO_6 octahedra and interlayer alkali metal cations (M^+) and water molecules.

Scheme 1



The sol−gel synthesis of potassium birnessite (K-OL-1) is outlined in Scheme 1. The addition of 50 mL of aqueous 0.38 M $KMnO_4$ to 20 mL of aqueous 1.4 M glucose or sucrose results in a rapid, exothermic reaction in which a brown gel is formed within 30 s. Water is periodically drained over the next 2 h as the gel undergoes syneresis. Drying at 110 °C for 24 h affords a brown xerogel. Calcination of the xerogel at 400−450 °C for 2 h produces impure K-OL-1 as a gray-black ash. After washing with water and drying at 110 °C, 1.85 g of pure K-OL-1 is isolated as a black solid. The X-ray powder diffraction pattern of the material contains diagnostic birnessite peaks with *d* spacings of 7.1 and 3.5 Å (Figure 2). Weaker peaks are also observed with *d* spacings of 2.5, 2.4, 2.2, 2.1, and 1.8 Å. The morphology of powdered sol−gel K-OL-1 was observed using scanning electron microscopy (Figure 3). The general appearance of sol−gel K-OL-1 is similar to that of K-birnessite prepared by the reaction of Mn^{2+} with $S_2O_8^{2-}$ in aqueous KOH,[19] but with a slightly smaller average particle size.

Elemental analyses is consistent with the general stoichiometry of $A_xMnO_{2\pm y}{\cdot}zH_2O$ found for OL-1 materi-

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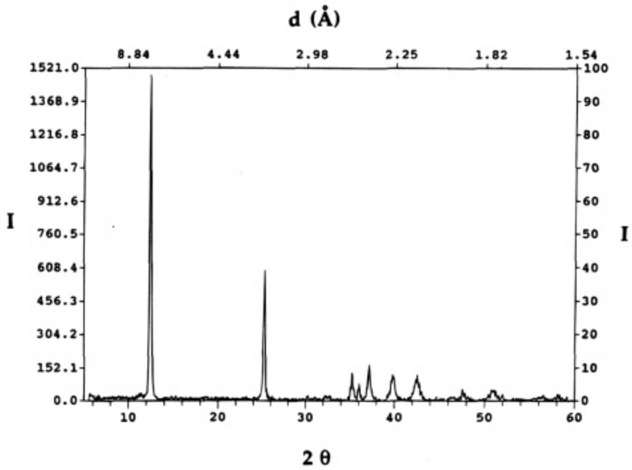

Figure 2. XRD pattern of sol−gel K-OL-1. Peak *d* spacings (Å) and peak indexes are as follows: 7.1 (002), 3.5 (212), 2.5 (144), 2.4 (161), 2.2 (253), 2.1 (324), 1.8 (316).

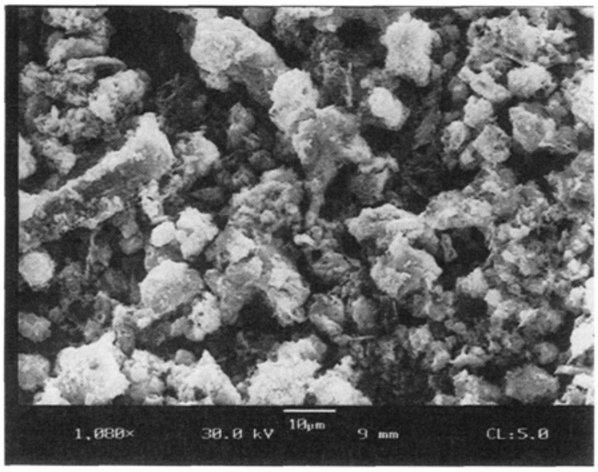

Figure 3. SEM photograph of powdered sol−gel K-OL-1.

als.[2] Analysis for K (10.9%) and Mn (54.9%) gives a K:Mn ratio of 0.279. This alkali metal:Mn ratio is very similar to that of synthetic sodium birnessites such as $Na_{0.29}MnO_{1.93}(H_2O)_{0.64}$.[20] However, the ratio is significantly smaller compared to other potassium birnessites that have K:Mn ratios as low as 0.21.[2,19] Iodometric titration was used in determining an average Mn oxidation state of 3.63.[21] An oxygen content of 34.2% was obtained by difference after calculating K and Mn percentages. Hydrogen content from interlayer water molecules was treated as negligible and carbon was analyzed at less than 0.5%. The analytical data were used to derive an empirical formula of $K_{0.28}MnO_{1.96}(H_2O)_{0.19}$. This formulation was based on weight percent values for K^+, $Mn^{3.63+}$, and O^{2-} and the assignment of excess O^{2-} to interlayer water molecules. Water content in OL-1 materials can be difficult to assess due to dependence on ambient humidity and slow hydration equilibrium.[22] This difficulty may be partially responsible for thermal gravimetric experiments showing a weight loss of 5% from 75 to 175 °C (assigned to water loss) whereas K-OL-1 as formulated from elemental analysis and oxidation state titration gives only 3.4% water.

K-OL-1 can be synthesized from a variety of polyalcohols in addition to glucose and sucrose. Reactions of $KMnO_4$ with ethylene glycol, glycerol, and poly(vinyl alcohol) also produce gels which may be converted to K-OL-1 upon drying and calcination. However, reactions of $KMnO_4$ with monoalcohols generate precipitates which afford Mn_2O_3 after calcination. The polyalcohols are believed to promote gel formation by cross-linking Mn metal centers during oxidation.

The permanganate cation plays an important role in reactions of MnO_4^- with sugars. Different cations were found to influence both gel formation and the nature of the final product.[23] Reactions of $Mg(MnO_4)_2$ with glucose yielded precipitates rather than gels, and Mn_2O_3 was produced upon calcination. Gels were obtained from reactions with $NaMnO_4$, but the product after calcination was mostly an unidentified manganese oxide having one major peak with a *d* spacing of 5.6 Å. Diffraction peaks for Na-OL-1 were also observed, but with much lower intensities. (The 7.1 Å birnessite peak was less than one-third that of the 5.6 Å peak.) The cation clearly affects the gel stage of the reaction and probably serves as a template for the K-OL-1 material during calcination. It is not yet clear why birnessite does not form in reactions with $Mg(MnO_4)_2$ and $NaMnO_4$. The case of Na^+ is particularly puzzling since Na-OL-1 is readily produced by alternative syntheses,[7,19,20] including one that uses a sol−gel procedure.[7] One possibility is that K^+ can complex with the gel in a way that Mg^{2+} and Na^+ cannot. Experiments are currently underway to address this issue.

K-OL-1 prepared by the sol−gel procedure is very stable compared to other synthetic OL-1 materials. Hydrothermal treatment at 160 °C for 2 days has no effect on sol−gel K-OL-1. By contrast, K-OL-1 prepared by Mn^{2+} oxidation with $S_2O_8^{2-}$ in aqueous KOH[19] is converted to manganite, Mn(O)OH, under identical conditions. Calcination of sol−gel K-OL-1 at 800 °C for 2 h has essentially no effect on its XRD pattern. Calcination at 1000 °C for 2 h results in partial degradation to Mn_3O_4 and other minor products that have not been identified by XRD. The stability of sol−gel K-OL-1 is impressive considering that some OL-1 materials are converted to tunnel manganese oxides such as hollandite[8] and cryptomelane[9] upon heating at 400−700 °C. Both of these less stable OL-1 materials were prepared by oxidation of Mn^{2+} using O_2 in aqueous base. Further examination of other synthetic K-OL-1 samples revealed that the thermal stability of sol−gel K-OL-1 was not unique. Stability at 800 and 1000 °C was also observed for K-OL-1 prepared from $Mn^{2+}/S_2O_8^{2-}/KOH$ mixtures,[19] though degradation to Mn_3O_4 is more pronounced. One possible explanation for the higher thermal stability is that K^+ pillars the manganese oxide layers in certain OL-1 samples. It was noted in SEM experiments that K-OL-1 samples from the sol−gel and $Mn^{2+}/S_2O_8^{2-}/KOH$ syntheses had similar

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particle morphologies (Figure 3) whereas OL-1 obtained from $Mn^{2+}/O_2/OH^-$ procedures were reported to form platelets.[20,24]

Thus far, attempts to quantitatively replace K^+ with other monovalent and divalent metal cations have been unsuccessful, and only a small fraction of K^+ has been exchanged in aqueous reactions at room temperature. In general, it has been observed that interlayer sodium cations in birnessite materials are weakly bound and easily exchanged.[25,26] Similar ion-exchange reactions are less facile with other interlayer cations.

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