Sol−Gel Route to the Tunneled Manganese Oxide Cryptomelane

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The sol−gel reaction between $KMnO_4$ and fumaric acid in a 3:1 mole ratio generates a flocculant gel that serves as a precursor to the tunneled manganese oxide, cryptomelane. The elemental composition of sol−gel cryptomelane has been determined to be $K_{0.12}MnO_{2.0}(H_2O)_{0.09}$. Further characterization has been performed using powder X-ray diffraction, scanning electron microscopy, and Auger electron spectroscopy. The sol−gel process is heavily dependent on reactant concentration. Solutions that are too concentrated produce the layered manganese oxide birnessite, whereas overly dilute reactions yield mixtures of cryptomelane and Mn_2O_3. The preference for cryptomelane over birnessite correlates with low potassium content in the gel. The sol−gel procedure for synthesizing cryptomelane is not easily transferred to the preparation of analogous manganese oxides with different tunnel cations. Reactions that employ permanganates other than $KMnO_4$ generally yield Mn_2O_3, with cryptomelane being a minor product at best. Thermal analyses of cryptomelane gels indicate that calcination proceeds through a series of stages that involve loss of water, loss of residual organics, conversion to cryptomelane, and finally degradation to Mn_3O_4. The extraction of potassium ions from sol−gel cryptomelane by various foreign cations is minimal, with the loss of K^+ being on the order of 10%.

Introduction

Cryptomelane is a microporous manganese oxide with the approximate stoichiometry of $K_{0.125}MnO_2$ (KMn_8O_{16}) and a structure consisting of 4.6 Å x 4.6 Å tunnels due to a 2 × 2 arrangement of edge-shared MnO_6 octahedra, Figure 1.[1−5] Potassium ions reside in the tunnels along with small amounts of water. The average manganese oxidation state of 3.88 reflects mixed valency from Mn(IV) and minor amounts of Mn(III).[2,3,6−8] Cryptomelane is related to a broader class of materials known as hollandites, which feature similar tunnel structures.[1−5,9,10] Manganese oxides in the hollandite group are isostructural and differ only by the tunnel cation. The term “hollandite” is used for this general classification of materials but also defines a specific manganese oxide with Ba^{2+} in the tunnels. In similar fashion, coronadite, manjiroite, and cryptomelane are defined as hollandites which contain Pb^{2+}, Na^+, and K^+.

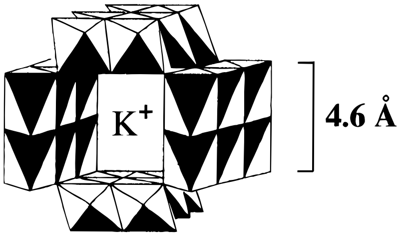

Figure 1. Illustration of the cryptomelane structure showing the 4.6 Å x 4.6 Å tunnels of edge-shared MnO_6 octahedra with K^+ inside the tunnels.

Cryptomelane is the most readily synthesized manganese oxide in the hollandite group, reflecting the effectiveness of K^+ in stabilizing the 2 × 2 tunnel structure. Cryptomelane can be prepared from layered manganese oxides such as birnessite by thermal[11−14] and hydrothermal[5] methods. Other common syntheses involve oxidation of Mn^{2+} in aqueous acid by reagents such as $KMnO_4$,[8,14] $K_2S_2O_8$,[15−17] and O_2.[18] Microporous manganese oxides with larger tunnels have also been synthesized. Todorokite, for example, has a

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3 × 3 (6.9 Å × 6.9 Å) array of edge-shared MnO_6 octahedra.[19-22] Romanechite is similarly formed with an asymmetric 2 × 3 tunnel.[23,24] Both these materials are prepared hydrothermally.

Manganese oxides with tunnel structures exhibit ion-exchange and molecular sieving properties[9,19] that make them interesting as potential zeolite analogues. Proposed applications of hollandite-type manganese oxides include heterogeneous catalysis and metal ion sorption. The materials also have potential use in battery technology. We use the term *octahedral molecular sieve* (OMS) to identify tunneled manganese oxides that have edge-shared MnO_6 octahedra as their basic structural unit.[19] Todorokite and cryptomelane have been designated OMS-1 and OMS-2, respectively.

We are exploring sol–gel routes to microporous manganese oxides,[25] with particular interest in realizing the advantages of sol–gel processing compared to other synthetic methods.[26-28] Sol–gel reactions are known for manganese oxides with layered structures, such as birnessite,[25,29-35] but analogous procedures for tunneled materials such as cryptomelane are relatively unknown. Bach and co-workers were the first to discover a sol–gel route to birnessite-type manganese oxides, using reactions of concentrated $KMnO_4$ with fumaric acid (*E*-butenedioic acid).[29] We similarly developed a sol–gel synthesis of birnessite from reactions between $KMnO_4$ and organic reducing agents such as glucose.[25] We learned from our reactions that concentration plays a major role in defining the types of gels and manganese oxides produced. This observation led us to examine related chemistry in other sol–gel systems.[36] Here we report the study of a dilute reaction between $KMnO_4$ and fumaric acid, the first sol–gel synthesis of a tunneled manganese oxide, cryptomelane.[37]

Experimental Section

Chemicals. Potassium permanganate (Janssen) and fumaric acid (Aldrich) were obtained as reagent grade chemicals and used as received. Other chemicals were likewise used without further purification. All reactions were carried out using distilled deionized water (18 MΩ) from a Barnsted Nanopure II purifying system.

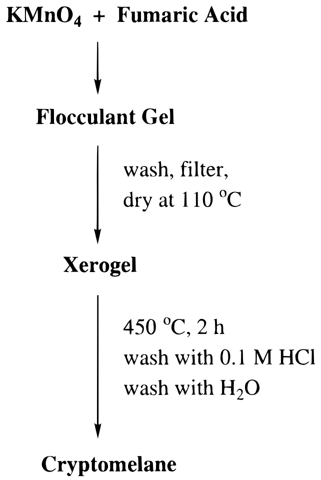

Figure 2. Schematic diagram of the sol–gel synthesis of cryptomelane.

Synthesis of Cryptomelane. A 0.78-g (6.7 mmol) sample of solid fumaric acid was added to a stirred solution containing 3.16 g (20 mmol) of $KMnO_4$ dissolved in 200 mL of water. The reaction proceeded with mild effervescence followed by the appearance of a brown sol within a few minutes. After 30 min, the sol evolved into a flocculant brown-black gel. The gel was allowed to settle and after 1 h was isolated by filtration and washed four times with 100 mL of water. A black xerogel formed after drying at 110 °C overnight. Calcination of the xerogel at 450 °C for 2 h yields cryptomelane as a hard, black solid. The product was pulverized, washed three times with 0.1 M HCl, and then washed three times again with distilled deionized water. After drying at 110 °C, a typical isolated yield was 1.8 g.

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

Characterization. Powder X-ray diffraction (XRD) data were obtained with a Scintag 2000 PDS X-ray diffractometer using Cu Kα radiation. Samples were spread out on glass slides and scanned at 5° 2θ/min. The beam voltage and beam current were 45 kV and 40 mA, respectively. Electron microscopy was carried out using an AMRAY Model 1810 D scanning electron microscope. Auger electron spectroscopy was performed with a Perkin-Elmer PHI 610 scanning Auger microprobe. The thermogravimetic analytical data were obtained using a Perkin-Elmer TGA-7 system under a nitrogen atmosphere. Thermally programmed desorption measurements were carried out as described in the literature.[38] Elemental analysis for metals was obtained using flame atomic absorption spectroscopy with a Perkin-Elmer Model 2380 AA. The elemental analysis for carbon was performed by Galbraith Laboratories. The average oxidation state of manganese was determined by iodometric titration.[39]

Results and Discussion

Cryptomelane Synthesis. The sol–gel synthesis of cryptomelane is shown schematically in Figure 2. The exothermic reaction between aqueous 0.1 M $KMnO_4$ and solid fumaric acid (*E*-butenedioic acid) in a 3:1 mole ratio generates a brown sol that congeals into a floccu-

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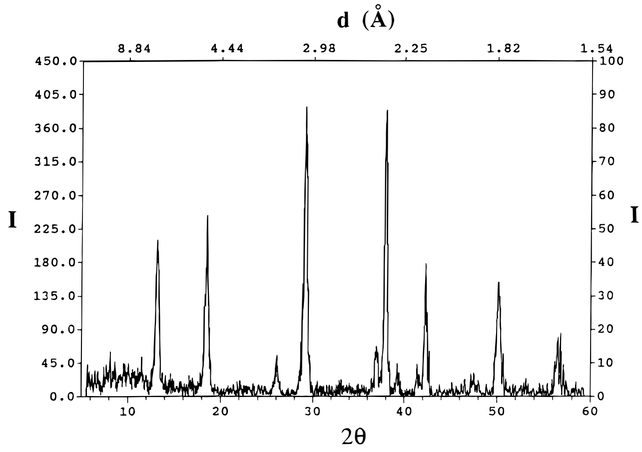

Figure 3. Powder X-ray diffraction pattern of sol–gel cryptomelane.

lant gel within 30 min. The fragmented nature of the gel allows it to be washed with water before drying. Calcination of the resulting xerogel at 450 °C for 2 h yields a crude cryptomelane sample which is purified by sequential washings with 0.1 M HCl and distilled deionized water. A similar reaction occurs between $KMnO_4$ and maleic acid (*Z*-butenedioic acid).

The powder X-ray diffraction (XRD) pattern of sol–gel cryptomelane shows sharp peaks and no evidence of other phases (Figure 3). The XRD pattern is in excellent agreement with XRD results obtained for non-sol–gel cryptomelane materials.[14] Scanning electron microscopy reveals well-defined particles with smooth faces and overall dimensions that are dependent on the extent of grinding (Figure 4). The morphology is significantly different from the finer needlelike appearance of cryptomelane prepared by reflux methods.[14]

An empirical formula of $K_{0.12}MnO_{2.0}(H_2O)_{0.09}$ has been determined for sol–gel cryptomelane from elemental analyses and manganese oxidation state data. The potassium (4.9%) and manganese (59.7%) compositions were obtained using atomic absorption spectroscopy, while the percent oxygen was calculated by difference on the assumption of negligible hydrogen content. Carbon was analyzed at less than 0.5%. An average manganese oxidation state of 3.87 was measured by iodometric titration. Cryptomelane is generally expressed with a stoichiometry of $K_{0.125}MnO_2$ (KMn_8O_{16}), which compares favorably with the sol–gel material. Thorough washing with dilute acid, as described in the synthesis, was necessary to remove surface-adsorbed potassium ions. Analytical data for unwashed samples and samples washed only with water revealed %K that were typically twice as high compared to acid-washed cryptomelane. Auger electron spectra of cryptomelane before and after acidic washing shows the removal of surface potassium (Figure 5). Adsorption of alkali-metal cations has been observed previously in syntheses of layered manganese oxides.[33,36]

Related Sol–Gel Reactions. Our synthesis of cryptomelane from $KMnO_4$ and fumaric acid is an outgrowth of sol–gel chemistry that we and others have developed for layered birnessite-type manganese oxides.[25,29–36] Bach and co-workers reported a similar reaction between permanganate and fumaric acid in a 3:1 mole ratio that yields birnessite instead of cryptomelane.[29,33,35] The critical difference between these two systems is the reactant concentration. Bach and co-workers used a 0.25 M $KMnO_4$ solution, which produced unfragmented gels. Our reactions use 0.10 M $KMnO_4$ and generate flocculant gels. We have made similar observations on a related sol–gel reaction between $KMnO_4$ and glucose.[36] In that system, highly concentrated solutions of $KMnO_4$ and glucose produce unfragmented gels leading to birnessite while more dilute solutions generate flocculant gels that yield cryptomelane and/or Mn_2O_3. Our sol–gel synthesis of cryptomelane presented here underscores the concentration dependence of the reaction between $KMnO_4$ and fumaric acid. Our use of dilute $KMnO_4$ solutions while maintaining the 3:1 mole ratio with fumaric acid has enabled us to modify the reaction of Bach and co-workers to generate flocculant gels that ultimately lead to cryptomelane instead of birnessite. However, if the reactions become too dilute, then mixtures of Mn_2O_3 and cryptomelane begin to form. Our results from reactions with various overall concentrations of $KMnO_4$ and fumaric acid are summarized in Table 1.

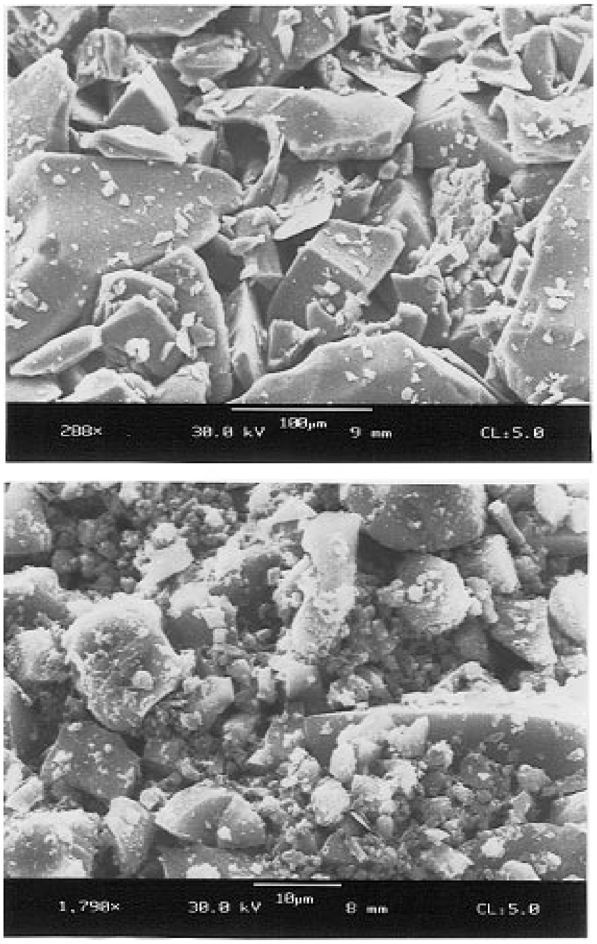

Figure 4. Scanning electron microscopy photographs of sol–gel cryptomelane.

Bach and co-workers also reported a non-sol–gel route to cryptomelane from $KMnO_4$ and fumaric acid which calls for an increase in the $KMnO_4$:fumaric acid ratio from 3:1 to 4:1 as well as an increase in acidity.[40] In our experience, the ratio of $KMnO_4$:fumaric acid exerts a relatively small influence on the synthesis of cryptomelane. Reactions with 0.1 M $KMnO_4$ and vary-

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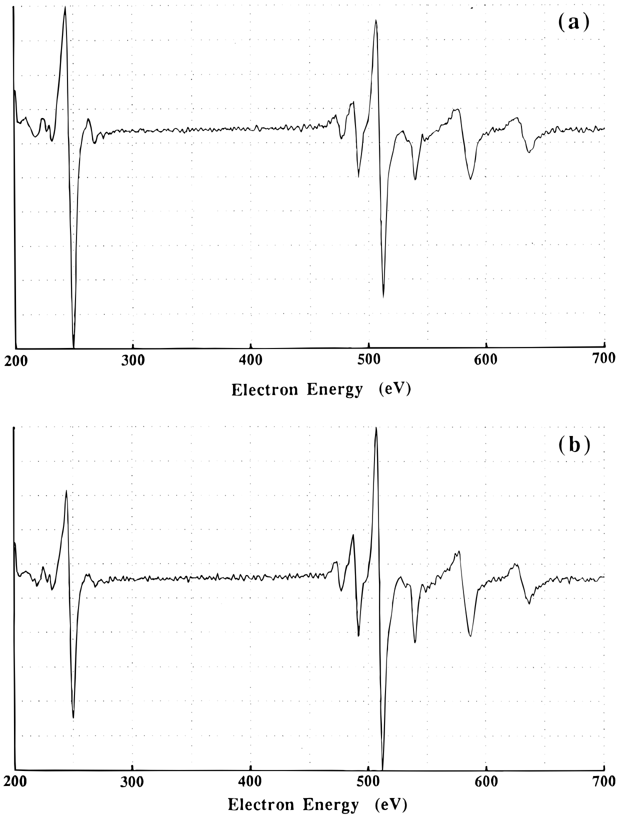

Figure 5. Auger electron spectra of sol−gel cryptomelane: (a) before washing with 0.1 M HCl and water; (b) after washing. The units of the vertical axis are dN(E)/dE. The peaks represent potassium (LMM: 252 eV), oxygen (KLL: 503 eV), and manganese (LMM: 542, 589, and 635 eV).

Table 1. Effects of Overall Reactant Concentration on Sol−Gel Reactions between $KMnO_4$ and Fumaric Acid

[$KMnO_4$] (M)	[fumaric acid] (M)	gel description	calcined product (450 °C, 2 h)
0.250	0.083	unfragmented	K-birnessite
0.100	0.033	flocculant	cryptomelane
0.050	0.017	flocculant	cryptomelane
0.020	0.007	flocculant	cryptomelane + Mn_2O_3

ing amounts of solid fumaric acid show that $KMnO_4$: fumaric acid ratios of 4:1 or less give flocculant gels that result in cryptomelane formation. Ratios above 5:1 give mixtures that do not progress beyond the sol stage. Changes in acidity or basicity, however, significantly alter the sol−gel products. Reactions of $KMnO_4$ and fumaric acid in 0.1 M HNO_3 produce precipitates that yield Mn_2O_3 while the same reactions in 0.1 M KOH generate flocculant gels that lead to birnessite.

We believe the sol−gel paths to cryptomelane and birnessite are determined by the potassium content of the manganese oxide gels. This hypothesis is supported by experiments in which mixtures of $KMnO_4$ and fumaric acid were subjected to a variety of reaction conditions and workup procedures (Table 2). Analyses of the resulting xerogels show a clear preference for cryptomelane at low potassium levels and small K/Mn ratios. Cryptomelane is obtained from xerogels with potassium contents on the order of 7% and K/Mn ratios of 0.2 or less. By contrast, birnessite is observed when the xerogels have potassium contents of 14% or more and K/Mn ratios greater than 0.4. Our findings are consistent with the fact that cryptomelane inherently has a much lower potassium content than birnessite.[41,42]

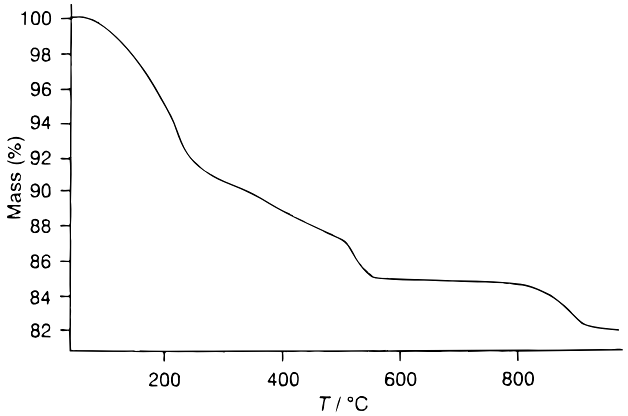

Figure 6. Thermogravimetric analysis of a cryptomelane xerogel.

Table 2. Xerogel Analyses and Manganese Oxide Products from Various Sol−Gel Reactions between $KMnO_4$ and Fumaric Acid

reaction conditions (gel treatment)	xerogel analysis		
	%K	K/Mn	product
0.100 M $KMnO_4$/0.033 M fumaric acid (filtered, washed)	7%	0.13	cryptomelane
0.100 M $KMnO_4$/0.033 M fumaric acid (filtered, unwashed)	18%	0.46	birnessite
0.100 M $KMnO_4$/0.033 M fumaric acid (unfiltered, unwashed)	23%	0.89	birnessite
0.100 M $KMnO_4$/0.033 M fumaric acid/ 0.1 M KOH (filtered, washed)	14%	0.51	birnessite
0.250 M $KMnO_4$/0.083 M fumaric acid (unfiltered, unwashed)	15%	0.45	birnessite
0.250 M $KMnO_4$/0.083 M fumaric acid (mechanically dispersed, filtered, washed)	7%	0.21	cryptomelane + Mn_2O_3

It is particularly illuminating that the unfragmented gels reported by Bach and co-workers can be converted from birnessite precursors to cryptomelane precursors after being dispersed and washed with water to extract K^+ (Table 2, last two entries). It is also noteworthy that while flocculant gels generally produce cryptomelane after washing, the flocculant gels obtained from reactions in KOH solution are able to retain a high potassium content and yield birnessite (Table 2, fourth entry).

Unfortunately, the sol−gel synthesis of cryptomelane from $KMnO_4$ and fumaric acid does not easily extend to other hollandite-type manganese oxides. Reactions of $LiMnO_4$, $NaMnO_4$, $Mg(MnO_4)_2$, and $Ca(MnO_4)_2$ with fumaric acid all result in the formation of Mn_2O_3 either exclusively or as the major product in mixtures with cryptomelane. Of the permanganates we studied, only $KMnO_4$ and $CsMnO_4$ generated hollandites without contamination from other phases.

Thermal Measurements. A thermogravimetric analysis of the cryptomelane xerogel is shown in Figure 6. The initial mass change between room temperature and 200 °C is due to loss of water. A subsequent weight loss from 200 to 500 °C is a result of the decomposition

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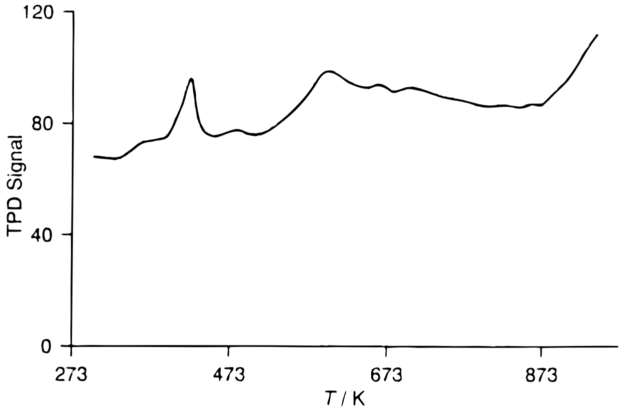

Figure 7. Temperature-programmed desorption for O_2 evolution of a calcined sample of sol−gel cryptomelane.

of residual organic fragments originating from fumaric acid. The small decrease from 500 to 550 °C represents the formation of cryptomelane. The final mass change from 800 to 900 °C is due to the conversion of cryptomelane into Mn_3O_4. The loss of water and organic species was detected by FT-IR spectroscopy.

Temperature-programmed desorption (TPD) results for O_2 evolution on a calcined sample of cryptomelane are shown in Figure 7. Integration of the TPD data reveals that between 273 and 873 K there is a loss of only 3% of the lattice oxygen atoms. The indication here is that the material is very stable over this temperature range.

Potassium-Ion Extraction. The extraction and insertion of cations in microporous solids are important processes that relate to potential applications in catalysis and chemical sorption.[9] Alkali-metal extraction has been especially well-examined for manganese oxides due to their promising nature as cathode materials for rechargeable lithium batteries.[8,31,34,43−48] Studies of extraction and insertion processes on a cation-poor form of Li hollandite have shown that the level of alkali-metal cation insertion is inversely related to ionic radius.[8,49] However, cation retention upon acid treatment shows the opposite relationship and is more favorable for larger cations.[8]

Potassium-ion extraction was examined for sol−gel cryptomelane using samples that were stirred in 1 M solutions of various nitrate salts for 24 h. The degree of extraction was assessed by the K/Mn ratio without distinguishing between ion-exchange and redox mechanisms.[8] The results displayed in Table 3 show poor extraction of potassium from sol−gel cryptomelane. In most cases, the decreases in %K and K/Mn ratio are just on the order of 10%. Only NH_4^+ gives a significant level of extraction at 42%. The extraction process was not improved with longer stirring times and higher temperatures. Acid treatment of conventionally prepared cryptomelane has been shown to extract nearly 50% of the potassium ions,[8] compared to only 12% for sol−gel cryptomelane.

Table 3. Potassium Ion Extraction from Sol−Gel Cryptomelane[a]

cation	%K	K/Mn	cation/Mn
K^+	4.9	0.12	0.12
H^+	4.3	0.10	
NH_4^+	2.8	0.07	
Li^+	4.4	0.11	
Na^+	4.3	0.10	0.008
Cu^{2+}	4.4	0.10	0.010

[a] Cation extraction is based on the depletion of K^+. The exchange cation was analyzed for selected elements as shown in the cation/Mn column above.

Conclusions

A sol−gel synthesis of the tunneled manganese oxide, cryptomelane, has been developed from the redox reaction between $KMnO_4$ and fumaric acid. Reactant concentrations are critical in this process since the layered manganese oxide, birnessite, forms when mixtures are too concentrated and substantial Mn_2O_3 contamination is observed for mixtures that are too dilute. Treatment of the gel prior to drying and calcination is also important since extraction of potassium ions from the gel favors cryptomelane over birnessite. The scope of the sol−gel reaction generally does not extend to other permanganates besides $KMnO_4$. Thus the procedure has not been successful in producing a wide variety of hollandite-type manganese oxides. The extraction of potassium ions from cryptomelane by exchange reactions with foreign cations appears to be relatively inefficient.

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