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Role of Cyclic Voltammetry in Characterizing Solids: Natural and Synthetic Manganese Oxide Octahedral Molecular Sieves

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Octahedral molecular sieves (OMS) having the todorokite (OMS-1) and hollandite (OMS-2) structures were used to modify carbon paste electrodes, and their cyclic voltammograms were recorded. The presence of Mn^{2+} in OMS-1 makes it electroactive; OMS-2 is not electroactive. Synthetic and natural todorokites showed very similar cyclic volammetric responses despite the difference in tunnel counter cations. Natural todorokites may contain different tunnel counter cations such as Mg^{2+}, Ba^{2+}, and K^+, while synthetic todorokite was prepared with Mg^{2+} as the counter cation in the tunnels. The different tunnel counter cations such as Mg^{2+}, Ba^{2+}, and K^+ do not influence the electrochemistry of either synthetic or natural todorokites. This observation suggests that the observed electroactivity of synthetic and natural todorokite may be due to framework Mn^{2+}. Todorokite synthesized in the presence of Cu^{2+} (Cu-OMS-1) was also used to modify carbon paste electrodes. Results indicate that Cu^{2+} in the Cu-OMS-1 is electroactive and mobile, but cannot be completely removed, suggesting that Cu^{2+} is located in the tunnels of Cu-OMS-1. OMS-1-modified carbon paste electrodes show an enhancement in the signal for Cu^{2+} ion in solution over that of unmodified electrodes. Cu^{2+} can exchange reversibly into and out of the tunnels of OMS-1 during cyclic voltammetric experiments.

Introduction

When preparing new compounds, it is useful to have rapid and convenient methods of characterizing and identifying the materials. In the present work a series of synthetic analogues of naturally occurring manganese oxide inclusion compounds were prepared. Cyclic voltammetry (CV) proved to be a rapid, convenient, and useful addition to the usual repertoire of techniques used to characterize and identify new solids. Electroactivity of manganese oxides, and their ion-exchange properties were both examined using CV.

Todorokite[1-6] and hollandite[7-11] are naturally occurring manganese oxide minerals[12,13] with tunnel structures, as shown in Figure 1. The basic unit structure is made of sheets of MnO_6 edge-sharing octahedra. Different manganese oxide minerals have different numbers of MnO_6 octahedra joined to form tunnels. Todorokite has the 3 × 3 structure; the tunnels are formed by linkage of three MnO_6 octahedra on each side. Using this terminology,

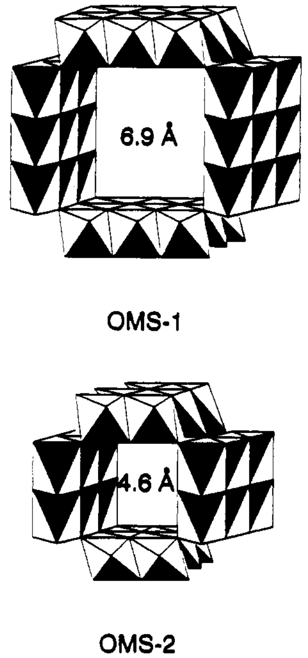

Figure 1. Structures of todorokite (OMS-1) and hollandite (OMS-2). The basic unit is the MnO_6 octahedron joined at the edges to form sheets and the tunnel structure. The tunnels in todorokite contain Mg^{2+}, Ba^{2+}, or K^+; while the hollandite tunnels may contain K^+, Ba^{2+}, and Pb^{2+} to compensate for the negative charge of the framework.

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hollandite has the 2 × 2 structure. There are other tunnel structures such as the 2 × 3 structure of psilomelane[14] and romanechite.

Counter cations and water are present in the tunnels of mixed-valent todorokite and hollandite to provide charge balance and stabilize the structure. Naturally occurring todorokite may contain Ba^{2+}, Mg^{2+}, and K^+ in the tunnels, where ion exchange can sometimes occur. The different counter cations inside the hollandite tunnels are the basis for the different names of hollandite-like minerals. Strictly, the term hollandite refers to the 2 × 2 mineral containing Ba^{2+} as the counter cation. Other naturally occurring hollandites contain K^+ (cryptomelane)[15,16] and Pb^{2+} (coronadite).[17]

In this study, we used manganese oxide minerals and corresponding synthetic octahedral molecular sieves to modify carbon paste electrodes. Our initial purpose was to use CV to distinguish todorokite and hollandite from other manganese oxide minerals. In addition, CV was used to determine whether transition-metal counter ions in synthetic manganese oxides were mobile, and therefore in the tunnels, or nonmobile in the framework. Solids such as alumina,[24] zeolites,[18–23] and pillared clays[25–28] have been used by others to modify electrodes. Some of these modified electrodes were made by mixing the solid with carbon paste (for example, see ref 18). Because these electrodes are easily prepared, robust, and reproducible, we used this method in the present study.

Experimental Section

Synthetic todorokite is referred to as OMS-1 and synthetic hollandite as OMS-2. OMS-1 and OMS-2 prepared in the presence of Cu^{2+} are referred to as Cu-OMS-1 and Cu-OMS-2, respectively. Synthesis of OMS-1,[30,31] Cu-OMS-1,[30] OMS-2,[29] and Cu-OMS-2[29] are described elsewhere. Modified carbon paste electrodes were made from carbon paste (BAS CP-W, Bioanalytical Systems) and todorokite or hollandite. The modifier and carbon paste were mixed using a mortar and pestle and packed into the tip of the BAS carbon paste electrode holder (3.0-mm diameter). The modified electrode contained from 20% to 30% manganese oxide by weight. Buffered electrolyte solutions were prepared from pHydrion Buffers (Micro Essential Laboratory, Brooklyn, NY) containing potassium phosphate (pH 7.0), sodium borate and carbonate (pH 10.0), and potassium biphthalate and sulfamic acid (pH 3.0). A BAS 100 electrochemical analyzer was used in cyclic voltammetric experiments. Electrolyte solutions were de-oxygenated by introducing argon gas for 10 minutes. Cyclic voltammograms were recorded using a modified carbon paste working electrode, SCE reference electrode, and Pt wire counter electrode, with scan rate of 100 mV/s.

Table I. Cyclic Voltammetric Response of Todorokite-Modified Carbon Paste Electrodes

		peak potentials (V vs SCE)	
modifier	electrolyte	cathodic	anodic
OSM-1	0.1 M KCl	−0.25	0.12
todorokite	0.1 M KCl	−0.27	0.20, 0.60, 1.00
Cu-OMS-1	pH 3.0	−0.20 to −0.32[a]	0.50 to 0.20[a]

[a] Multiple scans resulted in a shift in peak potentials.

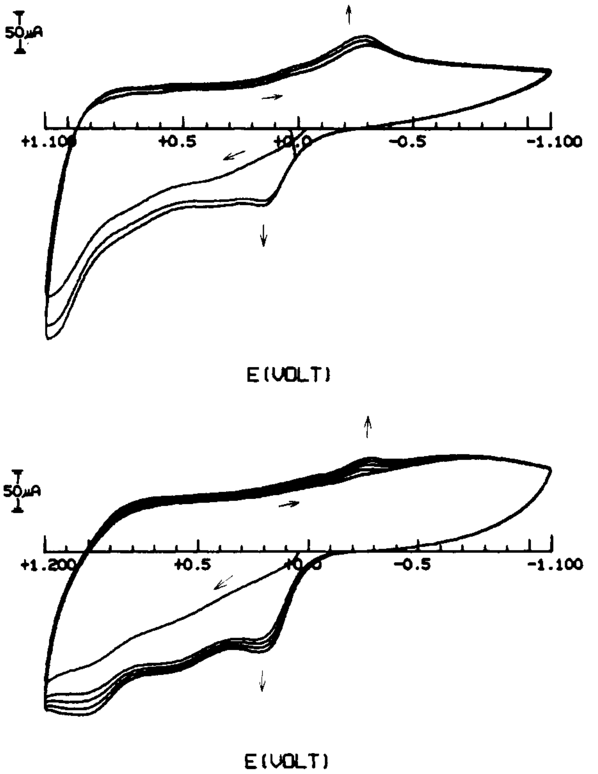

Figure 2. Cyclic voltammogram of (a, top) OMS-1 and (b, bottom) todorokite in 0.1 M KCl electrolyte vs SCE.

Results

CV of Todorokite and Hollandite. Experiments done on todorokite modified carbon paste electrodes show that todorokite is electroactive within the potential region examined and conditions used in this study. The OMS-1 modified carbon paste electrode showed an anodic peak at about +0.12 V vs SCE (see Table I) when CV was carried out in 0.1 M KCl as shown in Figure 2a. There was also a cathodic peak at −0 25 V, but in some cases, there was no distinct cathodic peak. Depending on the different OMS-1 samples prepared, this reduction peak was not consistently distinct. Otherwise, the shape of the voltammogram was highly reproducible for all the todorokite and OMS-1 samples we have studied. A cyclic voltammogram for natural todorokite is shown in Figure 2b. The shapes of voltammograms and peak potentials were sensitive to pH and choice of electrolyte.

For comparison, the cyclic voltammogram of a hollandite-modified carbon paste electrode is shown in Figure 3a. Neither hollandite nor OMS-2 (Figure 3b) showed distinctive electroactivity. Pyrolusite (MnO_2, Figure 3c)

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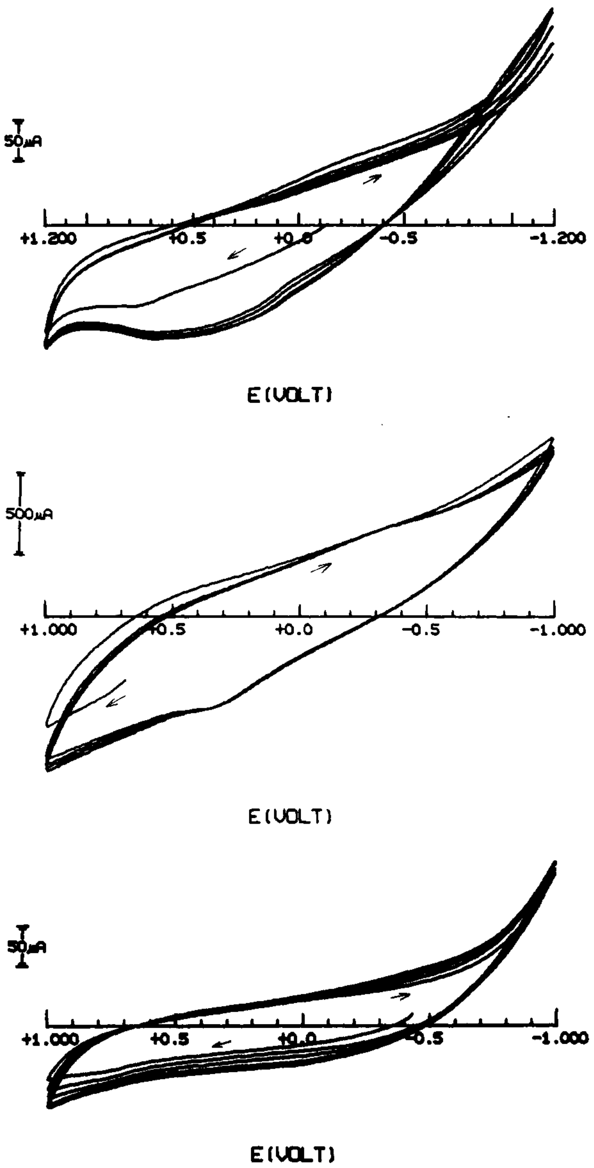

Figure 3. Cyclic voltammogram of (a) natural hollandite in pH 7.0 electrolyte solution. Synthetic hollandite at pH 7.0 was very similar to natural hollandite shown in (a). (b) Synthetic hollandite in 0.1 M KCl, and (c) pyrolusite (MnO_2) at pH 7.0.

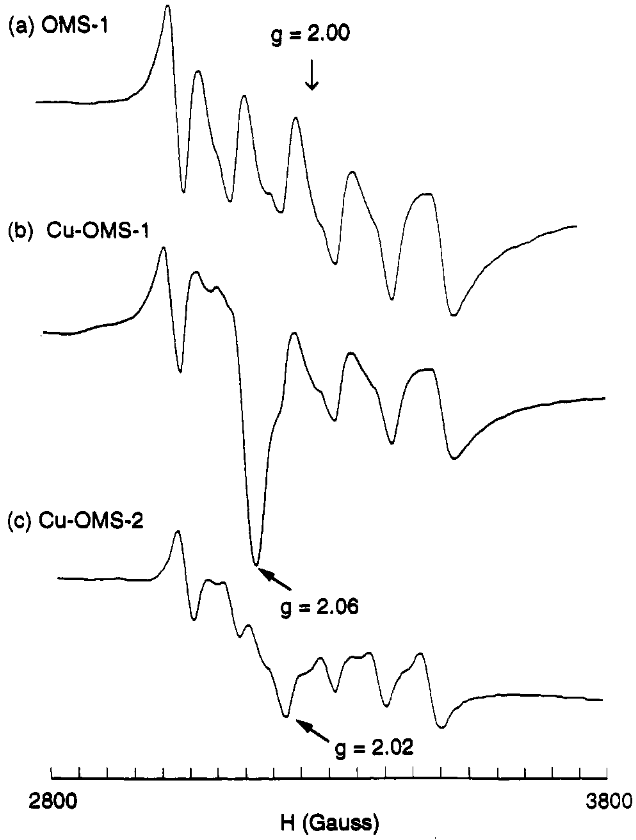

Figure 4. X-band electron paramagnetic resonance (EPR) spectra at 77 K of (a) OMS-1, (b) Cu-OMS-1, and (c) Cu-OMS-2. The six-line signals in (a), (b), and (c) are due to Mn^{2+}. The Cu^{2+} peak in Cu-OMS-1 (g 2.06) and Cu-OMS-2 (g 2.02) overlap the Mn^{2+} peaks.

Table II. EPR Parameters of Synthetic Todorokite and Hollandite

	Mn^{2+}		Cu^{2+}
	g	A^a	*g*
OMS-1	2.00	98	
Cu-OMS-1	2.00	98	2.06
Cu-OMS-2	2.01	85	2.02

[a] Hyperfine splitting constants in gauss.

and naturally occurring hollandite gave cyclic voltammograms that were similar to one another. These latter materials showed minimal electroactivity when cyclic voltammograms were recorded at neutral to acidic pH or in 0.1 M KCl.

EPR of OMS. Figure 4 shows the EPR spectra of OMS-1, Cu-OMS-1, and Cu-OMS-2. Results are summarized in Table II. OMS-1 and OMS-2 were synthesized in the presence of Cu^{2+} to determine the effect of doping Cu^{2+} into the OMS structure. Elemental analyses and electron paramagnetic resonance (EPR) experiments indicate that Cu^{2+} was incorporated into OMS-1 and OMS-2. The six-peak signals with a g value of 2.0 in Figure 4a–c indicate the presence of octahedral Mn^{2+} ion in OMS-1, Cu-OMS-1, and Cu-OMS-2. In Cu-OMS-1, the sharp peak at g 2.06 overlapping one of the Mn^{2+} peaks is due to the perpendicular component of the Cu^{2+} signal. The EPR spectrum of Cu-OMS-2 in Figure 4c shows Mn^{2+} (g 2.0, A 85 G; see Discussion) and Cu^{2+} (g 2.02). OMS-2 was EPR silent.

CV of Cu-OMS-1. CV was used to determine whether Cu^{2+} was in the framework or in the tunnels of Cu-OMS-1. Figure 5a shows the cyclic voltammogram of Cu-OMS-1 at pH 3.0. The cyclic voltammogram of Cu-OMS-1 modified carbon paste electrodes was pH dependent. At basic pH, no distinct Cu^{2+} peaks were found. The Cu^{2+} redox peaks appeared at pH 5.8, and well-defined peaks were also observed below pH 4.0. Figure 5b shows decreasing peak currents for Cu-OMS-1 modified carbon paste electrode at pH 3. Similar results were obtained at pH 4, and for unbuffered was 0.1 M KCl solution. Peak shapes and the drop in peak current are consistent with diffusion or migration of Cu^{2+} ions out of the Cu-OMS-1, followed by reduction at the surface of the electrode. The anodic peak is likely a stripping peak for oxidation of metallic copper.[18] There may also be some electron transfer among the various copper and manganese species that leads to an increase in current due to mediation of the electrode process (see Discussion).

The Cu-OMS-1-modified carbon paste electrode was placed in 500 mL of 0.1 M KCl solution, which was stirred for 2 days to replace mobile Cu^{2+} with K^+ by ion-exchange. A cyclic voltammogram using the same electrode at pH 3 showed a small anodic peak for copper (see Figure 5c).

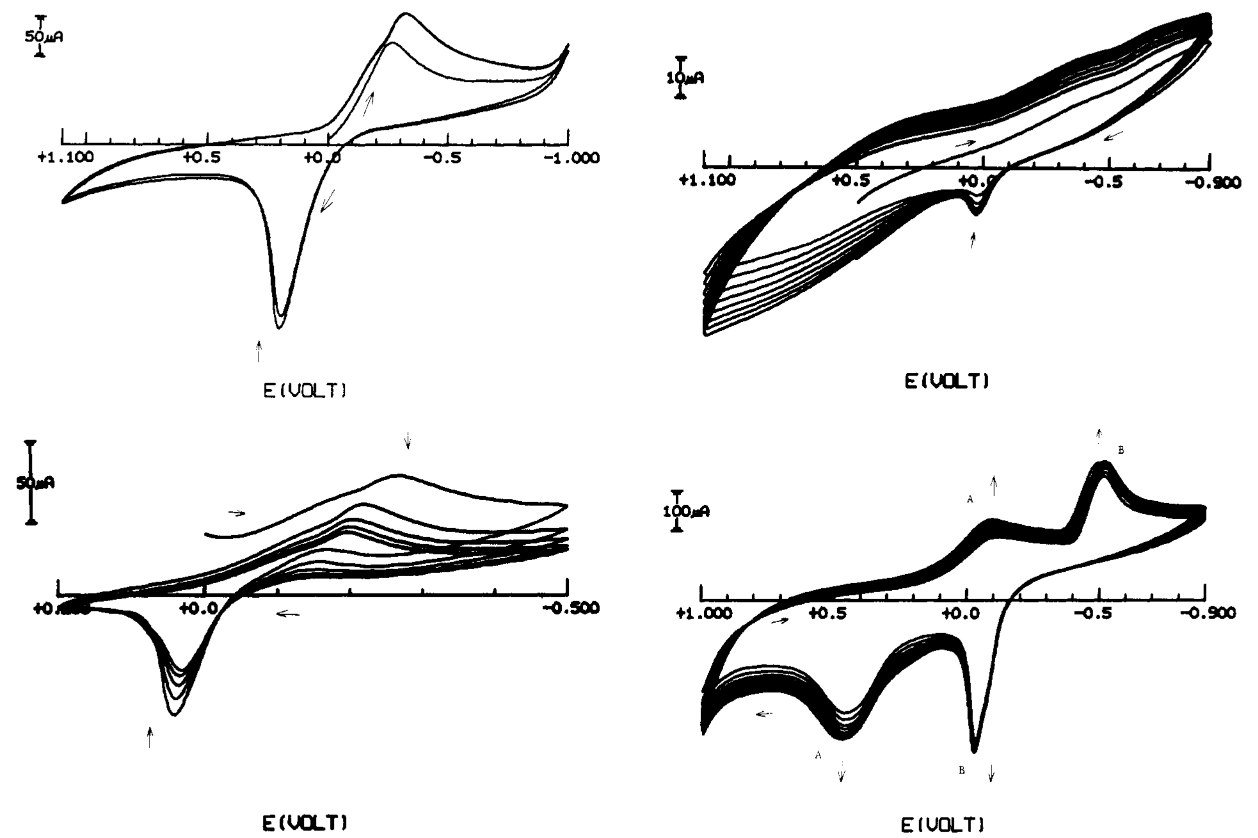

Figure 5. (a) Cyclic voltammogram of Cu-OMS-1-modified carbon paste electrode at pH 3.0 electrolyte vs SCE, scan rate 100 mV/s. (b) Same electrode scanned several times at 10 mV/s in pH 3.0 showing decreasing peak currents. (c) Cyclic voltammogram at pH 3.0 electrolyte and 100 mV/s after the same electrode was immersed in a stirred solution of 500 mL of 0.1 M KCl for 2 days showing decreasing anodic peak current at 0.0 V. (d) OMS-1-modified carbon paste electrode in 5 mM Cu^{2+} and 0.1 M CsBr showing increasing peak currents with multiple scans. Redox couples *A* and *B* are indicated (see Discussion and Table III).

This peak may arise from deposition of Cu^{2+} contributed to solution by the Cu-OMS-1 during the negative scan followed by stripping of metallic copper. Similar results were obtained when Cu-OMS-1 powders, washed with KCl solution, were used to prepare modified electrodes. Atomic absorption (AAS) analysis showed that the Cu content in some Cu-OMS-1 samples decreased by 2.50% due to washings. On the basis of the data described above, it is reasonable to conclude that all or most Cu^{2+} in Cu-OMS-1 is found in tunnels and is mobile, rather than being incorporated in the framework during synthesis.

CV of Cu-OMS-2. CV experiments using Cu-OMS-2 modified carbon paste electrodes do not indicate any sign of electroactivity of Mn^{2+} or Cu^{2+}. The voltammograms obtained were very similar to those recorded for OMS-2 and hollandite. This indicates that Mn^{2+} and Cu^{2+} formed in hollandite are not electroactive and are immobile.

Table III. Effect of Electrolyte Cation on Cu^{2+} Signal for OMS-1-Modified Carbon Paste Electrodes: Redox Couples *A* and *B*

	hydrated radii	redox couple *A*					redox couple *B*				
cation	(pm)[a]	E_{pa}[b]	i_{pa}[c]	E_{pc}[b]	i_{pc}[c]	E_{ave}[d]	E_{pa}[b]	i_{pa}[c]	E_{pc}[b]	inc[c]	E_{ave}[d]
Ca^{2+}	600	0.30	117	−0.08	108	0.11	0.00	275	−0.35	167	−0.18
Li^+	500–600	0.37	142	−0.12	142	0.13	0.02	225	−0.38	188	−0.18
K^+	300	0.38	183	−0.07	133	0.16	0.02	300	−0.35	192	−0.17
Cs^+	250	0.45	267	−0.10	154	0.18	−0.03	333	−0.52	304	−0.28

[a] Harris, D. C. *Quantitative Analysis*, 2nd ed.; W. H. Freeman: New York, 1987. [b] E_{pa} is initial anodic peak potential, E_{pc} is initial cathodic peak potential (V vs SCE). [c] i_{pa} is initial anodic peak current, i_{pc} is initial cathodic peak current (µA). [d] Average of E_{pa} and E_{pc} (V).

Electroactivity of Mn^{2+} in OMS-1. The mobility of Mn^2 in OMS-1 was also tested. Repeated washings of OMS-1 in KCl solution showed no sign of decrease in peak currents for the CV of OMS-1-modified carbon paste electrodes in 0.1 KCl solution. The overall shape of the voltammogram remained very similar to those presented in Figure 2. In fact, after several washings OMS-1 in 1.0 M KCl, the cyclic voltammogram of the OMS-1 modified electrode showed an increase in peak currents, when values were normalized to the amount of OMS-1 used to prepare the electrodes. This trend is opposite to what was found in the peak currents of Cu^{2+} after washing. Similar observations were noted even when the OMS-1 modified electrode was left in a stirred 100 mL of 1.0 M KCl solutions for 24, 48, and 72 h. It seems that the voltammetric response of OMS-1 modified electrodes is influenced by non-exchangeable Mn^{2+}.

Electrolyte Effects. CV of OMS-1 modified carbon paste electrodes was performed using electrolytes containing Ca^{2+}, Li^+, K^+, and Cs^+, in order of decreasing hydrated ionic radii. Table III shows the initial peak potentials and currents when modified electrodes containing 29% OMS-1 were immersed in 5 mM Cu^{2+} and 0.1 M of the respective electrolytes. Figure 5d shows a sample cyclic voltammogram when potential was cycled several times for OMS-1 modified electrode in 5 mM $CuSO_4$ and 0.1 M CsBr electrolyte.

V. Discussion

Electroactivity of Todorokite and Hollandite. It is likely that the presence of Mn^{2+} in the framework of todorokite and OMS-1 makes it electroactive. Using EPR, OMS-1[30,31] has been shown to contain octahedral Mn^{2+} ions while synthetic hollandite (OMS-2) does not contain Mn^{2+}. Others have shown that todorokite[4] and hollandite[3,7] minerals contain Mn^{4+} and Mn^{3+}, but only todorokite contains Mn^{2+}. Hollandite and OMS-2, which contain Mn^{3+} and Mn^{4+} are electroinactive. Pyrolusite (MnO_2), which contains Mn^{4+} but not Mn^{2+}, showed very similar CV responses to hollandite. Therefore, it is likely that Mn^{2+} in todorokite makes it electroactive. EPR and CV of Cu-OMS-2, however, revealed the presence of nonelectroactive Mn^{2+} and Cu^{2+}. The significance of finding Mn^{2+} in hollandite when doped with Cu^{2+} is further discussed elsewhere.[29] The smaller tunnel size may account for the nonmobility and nonelectroactivity of Mn^{2+} and Cu^{2+} in Cu-OMS-2. Todorokite contains Mg^{2+}, Ba^{2+}, and K^+ in the tunnels, while OMS-1 has Mg^{2+} as counter cation.[30,31] These counter cations are not electroactive under the conditions used in this study and do not affect the CV of todorokite and OMS-1. The formal potential for reduction of Mn(III) in Mn_2O_3 to give $Mn(OH)_2$ in the presence of water occurs at −0.08 V vs SCE at pH 7 (calculated for 25 °C from data given in ref 32). This observation is consistent with the possibility of electrooxidation of Mn(II) to Mn(III) in todorokite at a potential in the same range.

Electroactivity of Cu-OMS-1. When OMS-1 was synthesized in the presence of Cu^{2+}, CV was used to determine whether Cu^{2+} ions were in the framework or in the tunnel. CV results indicate that Cu^{2+} ions in Cu-OMS-1 are mobile and electroactive, and most probably are located in the tunnels. Figure 5a,b indicates that Cu^{2+} ions diffuse from Cu-OMS-1 into the solution. It is likely that reduction of Cu^{2+} ions occurs and Cu^0 plates onto the surface of the electrode. The Cu^0 is then stripped off upon reoxidation. This diffusion of Cu^{2+} and stripping of Cu^0 account for the sharp Cu^{2+} oxidation peak between 0.0 and 0.20 V, depending on the sample and conditions used in CV. Peak currents decreased upon repetitive cycling, indicating that Cu^{2+} ions migrate into the solution during each cycle. OMS-1 exposed to Cu^{2+} *in situ* gave one set of peaks that was qualitatively similar to those observed for Cu-OMS-1, again suggesting that Cu^{2+} can move freely into and out of the OMS-1 framework. A similar voltammetric response for Cu^{2+} was reported for Cu^{2+} in zeolite Y used to modify electrodes.[18]

In this study, the electroactive and mobile species are Cu^{2+} ions in Cu-OMS-1 modified carbon paste electrodes. There are two possible mechanisms that account for the behavior of a mobile electroactive probe in a porous modifier.[18] First, Cu^{2+} ions are reduced while inside the todorokite tunnel, or second, Cu^{2+} ions diffuse out and are reduced at the surface of the electrode. Both mechanisms rely upon the mobility of Cu^{2+} ions in the tunnel and the ability of cations to enter from the solution into the OMS-1 tunnel. The second mechanism seems to be the most probable in this case. The higher concentration of Cu^{2+} in the OMS-1 tunnels provides a diffusion gradient for movement to the surface of the electrode. The higher this diffusion gradient is, the higher the peak currents for the Cu^{2+} redox reaction.

Figure 5c suggests that some Cu^{2+} is bound tightly within OMS-1, in either the tunnels or the framework. This cyclic voltammogram was recorded after an attempt to remove all the ion-exchangeable Cu^{2+} ions by repeated washing with KCl solution. Washing of Cu-OMS-1 in KCl solution before using the Cu-OMS-1 to modify carbon paste electrodes resulted in a decrease in peak currents for the reduction of Cu^{2+}. This decrease was due to a drop in the concentration of Cu^{2+} ions inside the todorokite tunnels as a result of ion exchange with K^+. This decrease in the concentration of mobile Cu^{2+} was verified by atomic absorption spectroscopy. These data and those of Figures 2 and 5 suggest that CV can be used to follow ion exchange but cannot unambiguously distinguish cation locations (tunnel or framework) in OMS.

Electroactivity of Mn^{2+} in Todorokite. The mechanism to account for the electrochemistry of Mn^{2+} is different for that of Cu^{2+} ions in todorokite. In todorokite, CV shows that Mn^{2+} is not lost to the solution; the overall currents and shape of the voltammogram remain fairly similar even during several scans. It is possible that the observed electroactivity is due to framework Mn^{2+}. This is unusual; the electron transfer may possibly be enhanced by an increase in conductivity, relative to other molecular sieves examined electrochemically, due to the presence of mixed-valent manganese in todorokite. It is also possible that some Mn^{2+} ions are in the todorokite tunnels with restricted mobility because of the presence of other counter ions in the tunnels.

Two probable pathways of electron transfer in these tunnels are (1) mediated oxidation of framework Mn^{2+} ions by mobile, electroactive impurity cations, or (2) electron hopping among neighboring Mn^{2+} sites in the framework. Indeed, it is possible that electroactivity shown for Cu^{2+} in Figure 5 may include mediation by the manganese couple in the OMS-1 framework. Alternatively, Cu^{2+} may mediate electron transfer of the manganese couple. Recalling that currents for the manganese couple were enhanced by washing with KCl, the rate of electron transfer may be limited by mobility of charge-compensating ions. Potassium ions are expected to be more mobile than magnesium ions (ionic radius = 700–800 pm, reference in Table III), and might therefore enhance the rate of charge transer, evidenced by increasing currents.

The observed electroactivity of nonmobile Mn^{2+} in todorokite modified carbon paste electrode might be useful in electrocatalysis. The electrooxidation and reduction of Mn^{2+} may be coupled to other electrochemical reactions. Since Mn^{2+} is nonmobile, it can be regenerated every cycle with little or no loss. The tunnel pore of todorokite may provide size and shape selectivity of the reactants and products. Experiments are underway to examine the possible use of OMS-1 modified electrodes in electrocatalysis.

Electrolyte Effects. Figure 5d shows the cyclic voltammogram of an OMS-1 modified carbon paste electrode in 5 mM Cu^{2+} and 0.1 M Cs^+. Similar CV responses were recorded for Li^+, K^+, and Ca^{2+} electrolytes, showing increasing peak currents for Cu^{2+}. This indicates OMS-1 can preconcentrate Cu^{2+} ions from solution. There are two redox couples, labeled A and B in Table III. E_{ave} is the average of the anodic and cathodic peak potentials, and will be in the vicinity of the formal reduction potential when peak separations are small. The redox couple B, with the anodic stripping peak near 0.0 V, is believed to be due to the oxidation of metallic copper to Cu^{2+} ion. The Cu^{2+} ion is then dispersed in the solution, hence, the areas

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under the anodic and cathodic peaks are unequal. This stripping behavior of the Cu^{2+} redox peak is also observed in Cu–zeolites modified electrodes.[18]

The E_{ave} of the redox couple A observed when OMS-1 modified electrodes were immersed in Cu^{2+} solution varied from 0.11 to 0.18 V with Ca^{2+} to Cs^+ as the electrolyte. Except in the case of Cs^+, the anodic and cathodic peak areas were almost equal, and were probably due to the reaction

$$Cu^{2+} + e^- \rightleftharpoons Cu^+ \qquad -0.082\ \text{V (vs SCE)}^{32}$$

This redox couple was not observed for Cu-OMS-1- or Cu–zeolite-[18] modified electrodes, but was seen at unmodified carbon paste or platinum[18] electrodes in Cu^{2+} solution. This indicates that the CV response of Cu^{2+} from the solution at an electrode surface is different from the Cu^{2+} inside the pore structure of a modified electrode. Apparently, Cu^{2+} ions inside the modifier are only reduced to Cu^0, while Cu^{2+} from solution can be reduced to Cu^+ and Cu^0.

For Li^+, K^+, and Cs^+, redox couple B peak currents increased with decreasing hydrated radii (see Table III). Ca^{2+} was used to compare the effect of the divalent charge in the peak currents of Cu^{2+}. For the redox couple B of Cu^{2+} in the presence of Li^+, K^+, Cs^+, or Ca^{2+}, the ability of these cations to displace Cu^{2+} determines the magnitude of the signal. With one exception (see Table III) smaller hydrated ions displaced Cu^{2+} within OMS-1 more rapidly than larger ions, resulting in larger currents. This explains the larger Cu^{2+} peak current on immersion in Cs^+ solution rather than in K^+ or Li^+ (Table III). Data for Ca^{2+}-containing electrolyte solution were difficult to interpret for both processes, A and B. The anodic current for B, and anodic and cathodic currents for A were lower than for Li^+. However, the cathodic current for process B was higher than for Li^+, which has a similar hydrated radius (see Table III).

Cyclic voltammetric experiments yield information on kinetic effects such as the rate of displacement of Cu^{2+} and Mg^{2+} in Cu-OMS-1 by Li^+, K^+, Cs^+, or Ca^{2+}. The kinetic effects may follow the same trend as the relative distributions of the various ions at equilibrium,[18] or they may represent transient mobility factors. These issues will be investigated further.

The electroactive probes methylviologen, $Ru(NH_3)_5Cl^{2+}$, $Ru(NH_3)_6{}^{3+}$, and $Fe(CN)_6{}^{3-}$ were not preconcentrated by OMS-1- or OMS-2-modified carbon paste electrodes. The inability of OMS-1 (pore size 6.9 Å) and OMS-2 (pore size 4.6 Å) to accommodate these large probes in the tunnels is likely responsible for this observation.

Conclusions

Manganese oxide minerals with tunnel structures such as todorokite and hollandite can be used to modify carbon paste electrodes. The electrodes are robust and reproducible and are able to withstand stirring in solution for days. CV can be used to distinguish between todorokite and hollandite due to the presence of Mn^{2+} ions in todorokite. Todorokite is electroactive, while hollandite is not. The Mn^{2+} in todorokite is nonmobile, suggesting the presence of Mn^{2+} in todorokite tunnels with restricted mobility, or framework Mn^{2+}. Todorokite-modified carbon paste electrode enhances the Cu^{2+} signal, relative to an unmodified electrode, suggesting that Cu^{2+} is able to enter the todorokite tunnels. CV experiments on carbon paste electrodes modified with Cu-OMS-1 show that Cu^{2+} is electroactive and mobile, suggesting that Cu^{2+} is in the tunnels. Not all Cu^{2+} will exchange out, however, indicating the possibility of a small amount of electroactive Cu^{2+} ion in the todorokite structure.

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