

Phase Transitions and Ion Exchange Behavior of Electrolytically Prepared Manganese Dioxide

XIANG-MU SHEN* AND ABRAHAM CLEARFIELD†

*Department of Chemistry, Texas A&M University,
College Station, Texas 77843*

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Manganese dioxides were prepared electrolytically in the temperature range 10–95°C. The oxides prepared at 25°C or lower exhibited a high ion exchange capacity equivalent to one proton per two Mn atoms. Those prepared at higher temperatures exhibited correspondingly lower capacities and the 95°C preparation showed only surface exchange. The Li⁺ exchanged solid formed a spinel LiMn₂O₄ on heating and was converted to HMn₂O₄ on treatment with dilute acid. The protonated solid retained the spinel structure and showed a high specificity for Li⁺. A corresponding sodium ion exchanged phase yielded a birnessite-like phase on heating followed by treatment in boiling water. The sodium ion was exchanged with acid to yield a layered compound of composition H₄Mn₉O₁₈ · 7H₂O. It is suggested that λ-MnO₂ and Mn₇O₁₃ are deprotonated versions of the hydrogen ion exchanged species. It is further suggested that similar exchange reactions with insertion type compounds should lead to new types of inorganic ion exchangers. © 1986 Academic Press, Inc.

Introduction

Hydrous oxides are known to possess interesting ion exchange properties (1). Among the lesser known such oxides is hydrous manganese dioxide which has been shown to exhibit unusual ion selectivities (2). For example, if the hydrous manganese dioxide is loaded with Li⁺ and heat treated, its structure is altered so that the exchanger becomes highly selective for Li⁺ (3). The nature of the structural changes which occur as a result of this treatment are of interest in relation to the behavior of other hydrous oxides. It is known that ion exchange processes with other four valent oxides such as hydrous ZrO₂ and TiO₂ occur on

the surface of the exchanger (1, 4). Other hydrous oxides such as that of antimony, the so called polyantimonic acid, have been shown to possess a pyrochlore structure in which ions may occupy the A positions (4). So the question arises as to what type of structural changes can be induced in hydrous oxides to increase their specificity toward certain ions. We have undertaken to answer this question and have begun with a detailed study of the MnO₂ system.

A further incentive for carrying out this study is that Li⁺ has been inserted into manganese dioxide by reaction with organo-lithium compounds (5) or by the reaction of Li₂CO₃ with manganese oxides (6). The resultant product is a spinel of the type Li_xMn₂O₄. In fact similar insertion reactions have been carried out with other oxides (7a,b) and the phenomenon is common

* Visiting Scholar, People's Republic of China.

† To whom communications should be addressed.

enough to be considered a general reaction of spinel type oxides. As far as we know no one has compared the ion exchange process with insertion reactions, and this study was carried out with an eye to just such a comparison. Such reactions are important in considering the electrochemical behavior of MnO_2 .

Two types of manganese exchangers have been reported in the literature. The compound prepared by Tsuji and Abe by the interaction of KMnO_4 with MnSO_4 at 60°C was found to have the $\alpha\text{-MnO}_2$ structure (8). The formula proposed for this preparation was $\text{MnO}_2 \cdot 0.28\text{H}_2\text{O} \cdot 0.003\text{K}_2\text{O}$ or approximately $\text{Mn}_2\text{O}_{3.5}\text{OH}$. On this basis the exchange capacity should be 5.47 meq/g or slightly less to account for the excess water and K_2O . However, the observed exchange capacities for the alkali metals were much smaller than this value (8).

Russian workers prepared their manganese dioxide by an electrochemical technique (3, 9, 10) as did Kozawa (11). They proposed a formula similar to that shown above, viz. $(\text{MnO}_x)_2\text{OH}$ with $x = 1.70\text{--}1.75$. This formula would require either two different oxidation states for manganese when x was 1.70 or an increase in the hydroxyl content. The Russian workers found ion exchange capacities for Li^+ close to the theoretical values but those for larger ions to be much smaller. Furthermore they found that when the saturated lithium ion form was heated, followed by removal of Li^+ with acid, the exchanger was highly specific for Li^+ with a greatly reduced uptake for larger ions. It was therefore a further goal of this study to determine why the two manganese oxides exhibited such different behavior.

Experimental

Preparation of hydrous manganese dioxide. An electrolytic method was used for the preparation. The cell consisted of five

lead plates, each $8\text{ cm} \times 6\text{ cm} \times 1.5\text{ mm}$. Three of the plates served as negative and two as positive electrodes. The electrodes were connected in parallel and dipped into 500 ml of a solution 1.06 M in MnSO_4 and 2.04 M in H_2SO_4 . Current (1–3 A) and voltage (≈ 3 to 4 V) were controlled by a Hewlett–Packard 6291A dc power supply. Temperature was regulated by means of a constant temperature water bath fitted with a Haake-E12 stirrer circulator and a Precision Scientific electronic relay. Electrolysis was usually carried out for 12 hr and in one run for 50 hr. For temperatures below room temperature, an ice bath and cooling coil were used and cold water circulated continuously through the water bath. Following electrolysis the solid manganese dioxide was filtered off, washed several times with 1–2 M HNO_3 followed by exhaustive washing with distilled, deionized water and either air dried or dried in a desiccator over P_2O_5 for several days. The preparations are identified as EMDO-83xx-yy for electrolytic manganese dioxide, followed by an identification number 83xx. The last two digits (yy) identify the temperature of preparation. Preparations were carried out at 10, 25, 50, and 95°C .

Characterization of the preparations. Thermogravimetric analysis of each preparation was carried out with a Cahn Electrobalance (RG) in TG mode at a rate of $5^\circ\text{C}/\text{min}$. Infrared spectra were run with a Perkin–Elmer 580B spectrophotometer by the KBr disk technique on samples dried at 100°C . UV-visible reflectance spectra were obtained with a Varian-Cary 2300 spectrophotometer. A Hewlett–Packard 5950A ESCA unit was used to record the XPS spectra. The excitation radiation was $\text{AlK}\alpha$ ($h\nu = 1486.6\text{ eV}$). X-Ray powder patterns were run on a Scintag PAD-II diffractometer using $\text{CuK}\alpha$ radiation at a scan rate of $1^\circ\text{C}/\text{min}$. All pH measurements were carried out with a Fisher Accumet pH meter and Fisher combination electrode.

Ion exchange experiments. Equilibrium ion exchange titration curves were obtained by additions of 0.1 M (MCl + MOH) solutions to 0.25-g samples of the exchanger in sealed polyethylene bottles. The total volume to solid ratio was 100 ml/g and the hydroxide contents varied from 0.1 to 5.5 meq/g of exchanger. The containers were shaken in a thermostatted bath at $25 \pm 0.1^\circ\text{C}$ for 3 days and filtered. Analysis of the filtrate for metal ion content was done by atomic absorption and at the same time the pH of the filtrate was recorded. In some cases the solid was washed with 1 M HNO_3 and the total recovered M^+ determined for mass balance checks.

Dynamic titrations were also carried out in polyethylene bottles using 0.25 g of exchanger. To this solid was added 25 ml of 0.1 M MCl solution and the mixture shaken overnight. Then the pH was recorded and small increments of 0.1 M (MCl + MOH) added. The pH was read every 15 min and when two successive readings did not differ by more than 0.02 pH units another increment was added.

K_d values were determined at solution concentrations of 1×10^{-4} and 1×10^{-3} M/liter. The ratio of solution to solid was always 100 ml per gram of air dried solid. In all cases the TG curves were used to place the K_d and titration data on a per gram of water-free solid basis. Our definition of K_d is the conventional one, viz.

$$K_d = \frac{\text{meq M}^+/\text{g of exchanger}}{\text{meq M}^+/\text{ml of solution}}$$

Results

Characterization of the manganese dioxides. A combination of TGA, X-ray diffraction, ion exchange, and several spectroscopic methods were used to characterize the electrolytically prepared manganese dioxides. Although all the products were X-ray amorphous the behavior of the oxide

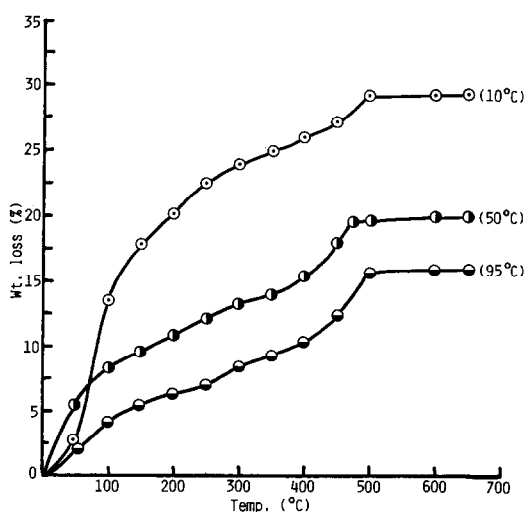


FIG. 1. Thermogravimetric curves for electrolytically prepared manganese dioxides (EMDOs). (○) EMDO-8301-10, (●) EMDO-8304-50, (◐) EMDO-8305-95. The plateau signifies formation of Mn_2O_3 .

was strongly dependent upon the temperature of preparation. This is illustrated in Fig. 1 which shows the TG curves for three samples of electrolytic MnO_2 . As the temperature of preparation was increased the total weight loss decreased. The upturn in the curves at approximately 450°C results from loss of oxygen and conversion of the solid to Mn_2O_3 with crystallization occurring at approximately 700°C . This phase was in turn transformed into Mn_3O_4 at higher temperatures.

Ion exchange titration curves, shown in Fig. 2 for the exchanger prepared at 10°C , were used to determine the amount of exchangeable protons present in the oxides as this value could not be distinguished from water of hydration in the TG curves. It is seen that the maximum uptake occurred with lithium ion. Lithium ion exchange results for several samples are collected in Table I. It is apparent that a drastic decrease in ion exchange capacity occurs between samples of MnO_2 prepared above and below 25°C .

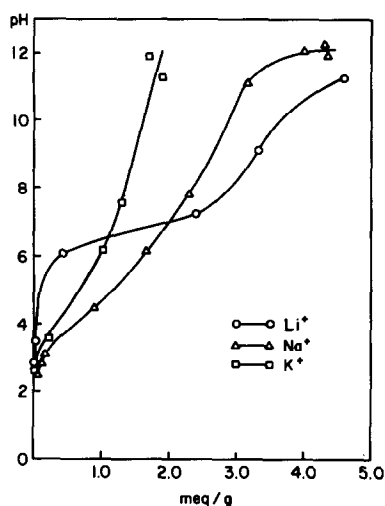


FIG. 2. Potentiometric titration curves for EMDO-8301-10. Titrants: (○) 0.1 M (LiCl + LiOH), (△) 0.1 M (NaCl + NaOH), (□) 0.1 M (KCl + KOH).

Determination of the amount of Mn³⁺ present in the electrolytically prepared samples was carried out by reduction to Mn(II) with arsenious acid followed by titration of the excess H₃AsO₃ with permanganate (12). Samples prepared below 25°C were found to contain 0.11–0.12 moles Mn³⁺ per formula weight whereas the samples prepared at 50 and 90°C contained none. Thus we may consider the general

formula to be (MnO_x)₂(OH)_y · zH₂O with the values of x, y, and z determined as just described. For the sample prepared at 10°C this representation then becomes (Mn_{0.89}^{IV}Mn_{0.11}^{III}O_x)₂(OH)_y · zH₂O. The total weight loss of one of the 10° samples (EMDO-8313-10) to the formation of Mn₂O₃ was 31.04%. This fixes the formula weight of the original air dried sample as 228.9, i.e., F.W. Mn₂O₃ / (1 - 0.3104). The exchange capacity of this sample was 4.37 meq/g (Table I) or 4.37 × 228.9 = 1 equivalent of exchangeable hydrogen ion per two manganese atoms. Thus, y = 1 and in order to balance the positive charge x is required to be 1.695. The value of z is then obtained from weight loss data as 2.65 and the steps in the dehydration are as follows:

- I—loss of 2.65 H₂O up to 200°C; calculated weight loss, 20.85%;
- II—Loss of 1 mole of hydroxyl as ½H₂O; calculated weight loss, 3.93%;
- III—Conversion of Mn_{1.78}^{IV}Mn_{0.22}^{III}O_{3.89} to Mn₂O₃ with loss of 0.89 moles of O (6.2% weight loss).

The sum total of these calculated weight losses is 31.0% as compared to an observed value of 31.04%. Formulas for the other preparations, derived in a similar fashion, are shown in Table I. Several points require further explanation. The two different ex-

TABLE I
WEIGHT LOSSES, LITHIUM ION EXCHANGE CAPACITIES, AND FORMULAS OF ELECTROLYTICALLY PREPARED MANGANESE DIOXIDE

Sample No.	Electrol. temp. (°C)	% Weight loss to 600°C	Exchange capacity (meq/g)	Proposed formula
EMDO-8301-10	10	28.84	4.64	(Mn _{0.89} Mn _{0.11} O _{1.69}) ₂ (OH) _{1.03} · 2.25H ₂ O
EMDO-8313-10	10	31.04	4.37	(Mn _{0.89} Mn _{0.11} O _{1.695}) ₂ OH · 2.65H ₂ O
EMDO-8311-20	20	29.65	4.47	(Mn _{0.88} Mn _{0.11} O _{1.685}) ₂ OH · 2.38H ₂ O
EMDO-8312-50	50	30.7	1.49	(MnO _{1.915}) ₂ (OH) _{0.34} · 2.82H ₂ O
EMDO-8304-50	50	19.9	1.62	(MnO _{1.92}) ₂ (OH) _{0.32} · 1.5H ₂ O
EMDO-8305-95	95	16.2	0	(MnO ₂) ₂ · 0.8H ₂ O

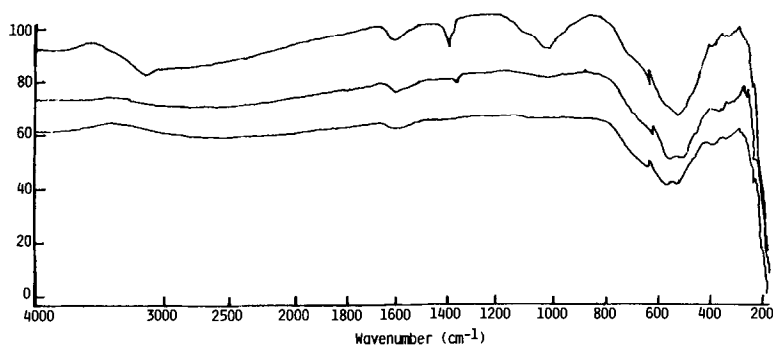


FIG. 3. Infrared absorption curves for EMDO-8301-10. Top curve—sample dried at 100°C; middle curve—sample dried at 240°C; bottom curve—sample dried at 390°C.

change capacities for the samples prepared at 10°C are due to the different water contents of the air dried samples. Otherwise these samples are similar. The two samples prepared at 50°C had different water contents. However, both of them gave ion exchange capacities which were equivalent to $\approx \frac{1}{2}$ of an OH group per two manganese atoms.

Infrared spectra were obtained in an effort to show the presence of the hydroxyl group in the samples prepared at the lower temperatures and the lack of this grouping in samples prepared at 95°C. The IR spectrum of EMDO-8313-10 dried at 100°C is shown in Fig. 3. The bands centered at 3110 and 1620 cm⁻¹ represent the water O—H stretching and bending modes, respectively. This water is apparently strongly hydrogen bonded as judged by the position of the band at 3110 cm⁻¹ or alternatively this band could represent (H₃O⁺). The water bands, as well as those at 1405 and 1030 cm⁻¹, are all absent in the spectrum of the sample dried at 250°C. In addition this sample lost its ion exchange capacity. Thus, both the water and the hydroxyl grouping are lost at this temperature.

Three samples (EMDO-8301-10, 8307-20, 8305-95) of the electrolytically prepared manganese dioxide were examined by

ESCA. The manganese 2*p* spectrum, shown in Fig. 4A, was similar for all three samples. For comparison purposes we have included the spectrum for MnO (Fig. 4B). It

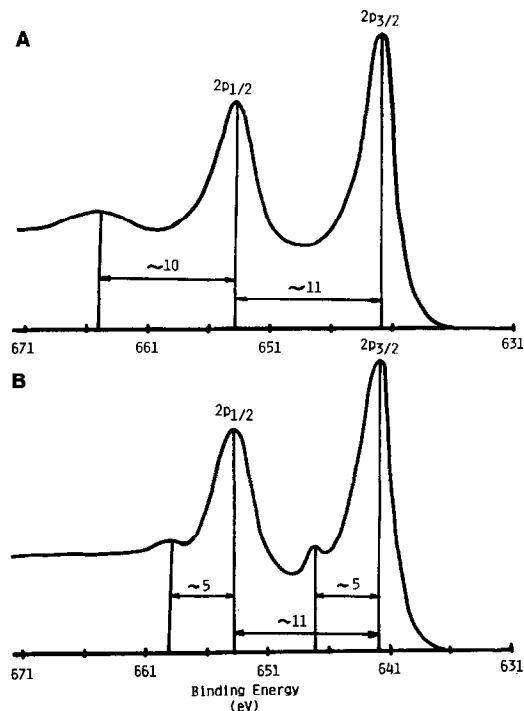


FIG. 4. ESCA spectra showing binding energies of Mn 2*p* electron in (A) electrolytically prepared manganese dioxide (EMDO) and (B) MnO.

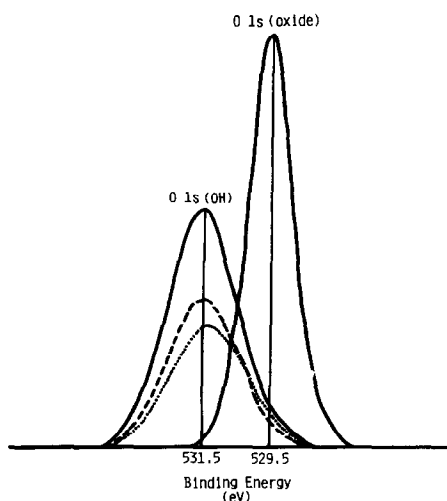


FIG. 5. ESCA spectra for O $1s_{1/2}$ electrons in EMDO-8301-10 (solid line), EMDO-8307-20 (dashed line), EMDO-8305-95 (dotted line).

is seen that the $\text{Mn}2p_{3/2}$ and $2p_{1/2}$ peaks for the EMDO and MnO occur at the same binding energies. However, MnO has satellite peaks 5 eV to higher energies than the main peaks. These satellites arise from shake-up processes (13). In Mn_2O_3 and Mn_3O_4 the satellite peaks are 10–11 eV higher in energy than the main peaks and this is the case for the EMDOs also. Thus we may conclude that no Mn^{2+} is present in the electrolytically prepared exchangers at the level of detection possible with the ESCA satellite peaks. In fact MnO_2 (pyrolusite) and Mn_2O_3 gave spectra almost identical to that of the EMDOs.

The O $1s$ electron (ESCA) spectra for the same three EMDOs are shown in Fig. 5. Two peaks with slightly different binding energies (529.5 and 531.5 eV) were observed. The peak at 529.5 eV had almost the same intensity for all three samples whereas the one at higher binding energy decreased as the temperature of preparation of the manganese dioxide exchanger increased. We interpret this observation in the following way. The peak at 529.5 eV

represents framework oxygen whereas the second peak is due to water and hydroxyl oxygen. As the temperature of preparation increases less hydroxyl and water are present in the product and this peak decreases in intensity. However a sample heated at 250°C and another heated at 300°C gave the same two peaks as shown in Fig. 5, but with the ratio about as shown for the dotted line in Fig. 5 relative to the peak at 529.5 eV. Thus, oxygen with two different coordinations must exist within the lattice structure. Mn_2O_3 exhibited an almost identical two peak spectrum whereas $\gamma\text{-MnO}_2$ exhibited only the peak at 529.5 eV in its XPS spectrum! Thus, it would appear that the EMDOs contain considerable Mn(III) . However, the oxidation reduction titrations do not agree with this hypothesis. This point needs further study.

Ion sieve formation. Titration curves for Li^+ such as those shown in Fig. 2 were used to fix the total ion exchange capacity. The measured capacity, 4.64 meq Li/g for EMDO-8301-10 (Table I) becomes 5.67 meq Li/g on a water-free basis. The comparable values for Na^+ and K^+ are 4.23(5.16) meq/g and 1.7(2.07) meq/g, respectively. In addition we note that the selectivity sequence below pH 6 is $\text{Na}^+ > \text{K}^+ > \text{Li}^+$ whereas above pH 7 it is $\text{Li}^+ > \text{Na}^+ > \text{K}^+$.

None of the exchanged forms showed any sign of crystallinity. However, when the lithium ion exchanged phase was heated it began to crystallize at about 220°C. At a heating temperature of 360°C three major reflections were present which allowed the crystallized phase to be identified (11) as the lithium spinel LiMn_2O_4 . This spinel form persisted up to heating temperatures of 960°C. That the spinel indeed contains Mn(III) is shown by the UV-visible spectra in Fig. 6. Curve a is the reflectance spectrum of the lithium spinel (heated to 520°C) which will be labeled $\text{MnIS(Li}^+)$, for manganese ionic sieve-lithium ion. It differs from the amorphous electrolytically pre-

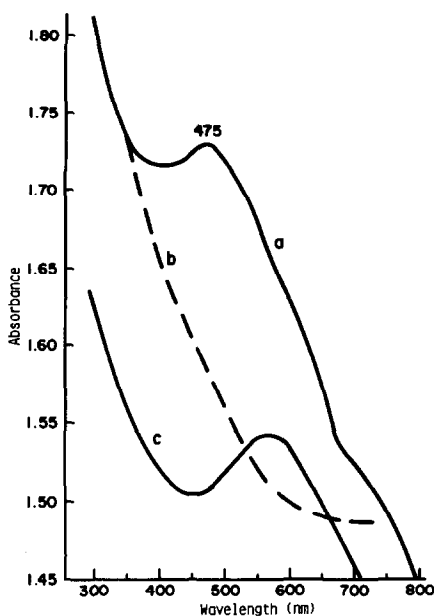


FIG. 6. UV-Visible absorption spectra of (a) the lithium spinel LiMn_2O_4 formed from the lithium ion exchanged EMDO at 520°C , Curve (b) is that of EMDO-8313-10, and curve (c) is that of the hydrogen form of the spinel, HMn_2O_4 .

pared ion exchanger (EMDO-8313-10), shown as curve b, by exhibiting a pronounced absorption band at 475 nm. Mn_2O_3 has a strong absorption band at 475 nm which is attributed to the ${}^5E_g \rightarrow {}^5T_{2g}$ transition (14). In the case of manganese(III) acetate this band occurs at 445 nm. Upon removal of the Li^+ from $\text{MnIS}(\text{Li}^+)$ with acid, the absorption band moves to 570 nm as shown in curve c.

Above 950°C another phase transition occurs with loss of oxygen to produce $\text{Li}_2\text{Mn}_4\text{O}_7$ in which all of the manganese is in the +3 state.

Washing the lithium spinel (prepared at 520°C) with 0.1 M HNO_3 removed the lithium ion completely and a hydronium ion form, still retaining the spinel X-ray pattern (d spacings 4.65, 2.43, and 2.02 Å versus 4.67, 2.47, 2.05 for the Li^+ form (15)), was obtained. The ion exchange behavior of the

hydrogen spinel $[\text{MnIS}(\text{H})]$ is dramatically different from that of the initial electrolytically produced hydrous oxide. This is shown by the titration curves of Fig. 7. These data verify the previous findings (3) that the foregoing heat treatment of the exchanger imparts a high specificity for lithium ion to the exchanger. Actual uptake capacities at pH 12 were 4.63, 0.35, and 0.21 meq/g for Li^+ , Na^+ , and K^+ , respectively, for the air dried exchanger containing 1 mole of H_2O . The formula for this ionic sieve, as determined from its TG curve (Fig. 8), is HMn_2O_4 . The first weight loss (to 350°C) is due to the split out of $\frac{1}{2}\text{H}_2\text{O}$. This is followed by the loss of $\frac{1}{2}\text{O}$ between 350 and 550°C . The final weight loss of 3.04% represents the conversion of Mn_2O_3 to Mn_3O_4 .

As the temperature of heat treatment of the lithium spinel increased the lithium ion became more tightly bound within the spinel structure. We have seen that the exchanger heated at 520°C retained essentially complete reversibility as regards $\text{Li}^+ - \text{H}^+$ exchange. In fact we showed this by cycling the exchanger four times. How-

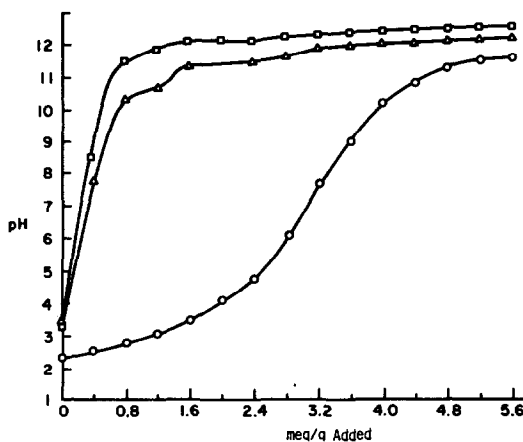


FIG. 7. Potentiometric titration curves for the hydrogen form of the spinel $\text{MnIS}(\text{H})$. Titrants: (O) 0.1 M ($\text{LiCl} + \text{LiOH}$), (Δ) 0.1 M ($\text{NaCl} + \text{NaOH}$), (\square) 0.1 M ($\text{KCl} + \text{KOH}$).

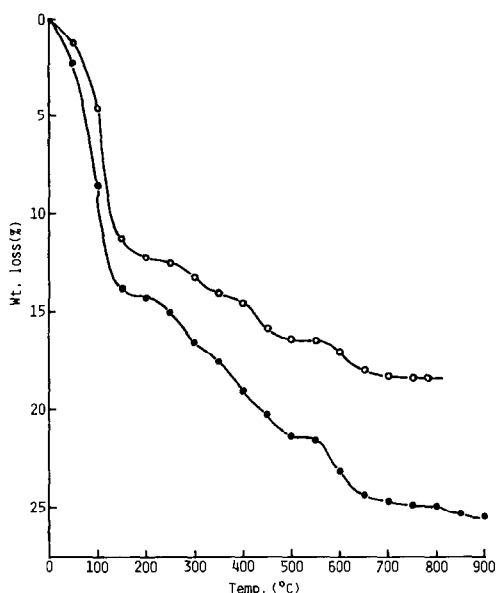


FIG. 8. Thermogravimetric weight loss curves for the hydrated sodium ion phase ISM(Na) (O) and the hydrated hydrogen form obtained from it ISM(H) (●).

ever, when the $\text{MnIS}(\text{Li})$ sample was heat treated at 640°C , its capacity for lithium ion exchange, in the hydronium ion form, was reduced to 3.92 meq/g and similarly at 900°C the capacity was only 3.3 meq/g. The highest observed ion exchange capacity (4.63 meq/g) is far short of the theoretical value of 5.72 meq/g.

The lithium spinel can also be prepared by heating MnO_2 with lithium carbonate (15). When this was done at a temperature of 520°C , the X-ray pattern resembled the product of Li^+ exchanged into the electrolytically prepared exchanger followed by heat treatment at the same temperature. The spinel prepared by the carbonate route retained Li^+-H^+ exchange reversibility. Thus, this synthetic procedure is a much more convenient path to the preparation of the lithium specific exchanger.

Sodium ion reactions. In the case of the sodium ion exchanged form of the exchanger (EMDO-8313-10) heating to 520°C

for 10 hr converted the amorphous gel into a new phase which exhibited X-ray powder reflections at $5.54 \text{ \AA}(100)$ and $2.76 \text{ \AA}(15)$. When this phase was boiled in water, it was converted to a birnessite-like phase [$d = 7.04(100)$, $3.53(2)$, $2.50(10)$, $2.39(15)$, and $2.12(10)$] (16). It has been formulated as $\text{Na}_4\text{Mn}_{14}\text{O}_{27} \cdot 9\text{H}_2\text{O}$ (17). However, analysis of two of our samples gave 8.4% Na, 47.24% Mn, $\text{Na}/\text{Mn} = 0.425$, and 9.5% Na, 49.44% Mn, $\text{Na}/\text{Mn} = 0.459$. The birnessite formula given above requires $\text{Na}/\text{Mn} = 0.285$. In order to see if $\text{Na}_4\text{Mn}_{14}\text{O}_{27}$ could be synthesized by a direct method we heated a mixture of sodium carbonate and EMDO-8313-10 in a ratio of Na to Mn of 0.285. At 500°C the product obtained was $\text{Na}_{0.2}\text{MnO}_2$ while heating at 830°C produced $\text{Na}_{0.44}\text{MnO}_2 + \text{Mn}_2\text{O}_3$ (18). When the amount of sodium carbonate was increased so that Na/Mn was 0.5 a mixture of $\text{Na}_{0.2}\text{MnO}_2$ and the phase with the 5.54-\AA interlayer spacing was obtained. Finally increasing the ratio to 1 produced only the 5.54-\AA phase at 520°C . However, at about 900°C $\alpha\text{-NaMnO}_2$ was the final product.

We chose to study the phase obtained at 500°C which, when boiled in water, gave the birnessite-like phase. It will be referred to as ISM(Na) and its TGA curve is shown in Fig. 8. The first plateau at $\approx 150^\circ\text{C}$ (11.78% weight loss) is due to loss of water with contraction of the interlayer spacing to 5.61 \AA . This contraction is difficult to detect since exposure of the solid to air allows it to rehydrate. There is another slight break at $\approx 350^\circ\text{C}$ and a more pronounced one at 500°C . In this temperature range there appears to be a topotactic transformation from the nearly anhydrous phase ($d = 5.61$ and 2.41 \AA) to the original anhydrous phase with d spacings of 5.54 and 2.76 \AA . The final weight loss (at 700°C) amounts to 2.2%, but on cooling to room temperature, the solid regains 1.7% oxygen to yield at room temperature $\text{Na}_{0.44}\text{MnO}_2$ plus Mn_3O_4 .

Washing our synthetic birnessite with

0.1N HNO₃ converted it to the acid form. Its X-ray powder pattern corresponded to that given by Giovanoli *et al.* (19) who represented it as Mn₇O₁₃ · 5H₂O based on analytical data. This formula would require that some oxidation of manganese take place in the washing step. However, we have represented the acid form as H₄Mn₉O₁₈ · 7H₂O (M.W. = 912.6) to accord with thermal and ion exchange data. The TG curve for this compound is shown in Fig. 8. At the first plateau (150°C) a 13.8% weight loss was recorded which corresponds to the loss of all the water. In the next step a weight loss of 7.64% was observed and the product (at 514°C) was Mn₂O₃. This weight loss is attributed to the loss of 2.5 moles of atomic oxygen (or 1½ O₂) and approximately 2 moles of water which amounts to 8.33% weight loss. For reasons given below we postulate that about 20% of the protons are retained to accord with the actual weight losses. In the final stage the Mn₂O₃ is converted to Mn₃O₄ with the loss of 1½ moles of (atomic) oxygen amounting to a 2.63% weight loss. However, the actual observed weight loss is 3.42% and we attribute this higher value to the condensation of the remaining hydroxyl groups.

Ion exchange behavior of H₄Mn₉O₁₈ · 7H₂O. The ion exchange titration curves for Li⁺, Na⁺, and K⁺ on the acid form of birnessite is shown in Fig. 9. It is seen that initially the affinity sequence is K⁺ > Na⁺ > Li⁺ but the curves pass through a reversal point at about 50% loading and then the sequence is reversed to Li⁺ > Na⁺ > K⁺. The exchange capacity for Li⁺, determined by a static method, amounted to 4.38 meq/g which is the same value as observed at the top of the titration curve. The theoretical value of the proposed formula is also 4.38 meq/g. Given this high exchange capacity it is evident that the formulation of the acid form as a nonprotonated phase is incorrect. The layered nature of the acid form was demonstrated by its intercalation of butyl-

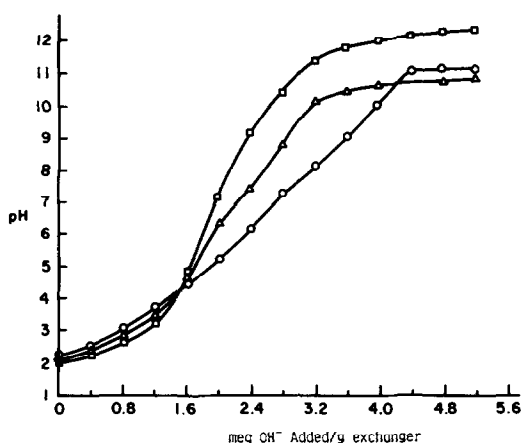


FIG. 9. Potentiometric titration curves for ISM(H), H₄Mn₉O₁₈ · 7H₂O. Titrants: (O) 0.1 M (LiCl + LiOH), (Δ) 0.1 M (NaCl + NaOH), (□) 0.1 M (KCl + KOH).

amine. About 1.8 moles of amine were incorporated and the interlayer distance enlarged to ≈15 Å.

The result of a mixed ion uptake experiment proved interesting. A sample of EMDO-8311-20 was treated with a mixed LiOH-NaOH solution in 2:1 ratio sufficient to obtain saturation of the exchanger (1.5 moles M⁺ per mole of Mn). The solid was then heated to 800°C and found to form two separate phases: The lithium spinel and the unidentified sodium ion precursor phase to birnessite. These two phases, on treatment with water, behaved as a mixture of two separate phases. The sodium ion phase took up water to produce birnessite, but the lithium spinel remained unchanged. Thus, complete segregation of the two ions in separate phases was apparently achieved.

K_d values. Distribution coefficients for the two types of ion exchangers [EMDOs and ISM(H⁺)] were determined at alkali metal concentrations of 10⁻³ and 10⁻⁴ M. In Table II are collected values for the electrolytically prepared exchanger EMDOs-8301-10 and it is seen that for both concentrations the selectivity sequence is K⁺ > Li⁺ > Na⁺. This sequence is different than the

TABLE II
DISTRIBUTION COEFFICIENTS, K_d , AND SEPARATION FACTORS, α_B^A , FOR
ELECTROLYTICALLY PREPARED MANGANESE DIOXIDES (EMDO) ($T = 25^\circ\text{C}$)

Exchanger	Solution conc. (M/l)	Ions	Na ⁺	Li ⁺	K ⁺
EMDO-8301-10	10 ⁻³	Uptake (meq/g)	0.0005	0.014	0.052
		K_d	4.8	15.4	110
		α_B^A	3.2	7.2	
EMDO-8301-10	10 ⁻⁴	Uptake (meq/g)	0.0006	.0011	0.0087
		K_d	6.5	10.9	751
		α_B^A	1.7	68.9	
EMDO-8305-90	10 ⁻⁴	Uptake (meq/g)	9.7×10^{-4}	0.004	0.0094
		K_d	10	59.6	1370
		α_B^A	6	23	

one obtained from the titration curves. However, the loading is so low that the number of sites available to the cations is many times the loading. Thus site accessibility or sieving effects do not come into play for such small loads as they do for macroloadings. Exchange may principally be taking place at the surface (see below).

Another factor to consider is the effect of pH on K_d . In Fig. 10 we have plotted $\log K_d$ as a function of pH for K⁺ uptake. The solution phase was 10⁻⁴ M KCl. The slope of the line is +0.98 as required for reversible exchange of unipositive ions. Surprisingly, measurable K_d values were obtained for EMDO-8305-90, a sample which showed no

measurable macroexchange capacity. Here we see relatively large K_d values. Presumably the surface of this solid contains enough hydroxyl groups to exhibit microlevels of exchange.

Distribution coefficients for the ISM(H⁺) exchanger or spinel type are shown in Table III. Here the trend is clear. K_d values for K⁺ and Na⁺ are low and decrease with increasing pH. On the other hand K_d values for Li⁺ are higher and remain relatively constant over the entire pH range examined.

In Table IV we have collected Li⁺-Na⁺ separation factors for solutions of increasing sodium-lithium ratio. It is seen that the

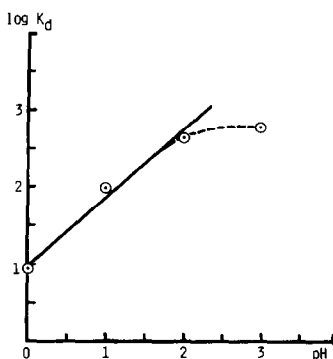


FIG. 10. The effect of pH on K_d in 10⁻⁴ M KCl.

TABLE III
DISTRIBUTION COEFFICIENTS AND SEPARATION
FACTORS FOR THE SPINEL HYDROGEN FORM HMnO₂
(ISM(H⁺))

	Ions	K ⁺	Na ⁺	Li ⁺
pH = 4.1	K_d (ml ³ · g ⁻¹)	11.8	18.9	107.3
	α_B^A		1.6	5.7
pH = 5.1	K_d (ml ³ · g ⁻¹)	4.5	5.5	129.6
	α_B^A		1.3	23.5
pH = 4.1	K_d (ml ³ · g ⁻¹)	3.7	5.3	127.1
	α_B^A		1.4	28.9
pH = 4.1	K_d (ml ³ · g ⁻¹)	2.7	4.4	89.3
	α_B^A		1.6	20.3

TABLE IV
ION UPTAKE AND SEPARATION FACTORS ($\alpha_{\text{Na}^+}^{\text{Li}^+}$) FOR H-FORM IONIC SIEVE AS A FUNCTION OF THE
 Na^+/Li^+ RATIO IN SOLUTION

Experimental conditions					Results		
Exp. No.	pH	Initial solution concentrations (M)		Na^+/Li^+ (ion)	Ion uptake (meq/g)		Separation factor $\alpha_{\text{Na}^+}^{\text{Li}^+}$
		Na^+	Li^+		Li^+	Na^+	
5	12.6	5×10^{-2}	5×10^{-2}	1:1	4.0	0.21	3.2×10^1
6	11.4	5×10^{-1}	5×10^{-2}	10:1	3.6	0.22	3.3×10^2
7	11.5	5.0	5×10^{-2}	100:1	3.3	0.34	1.7×10^3
3	10.3	5.0	5×10^{-3}	1,000:1	2.8	0.57	1.0×10^4

values increase by approximately an order of magnitude for every 10-fold increase in the ratio. Although the Na^+ uptake increases and the equilibrium uptake of Li^+ decreases as the solution becomes richer in sodium, Li^+ is always the preferred ion. An interesting observation is the increased sodium ion content, 0.57 meq/g, over that obtained when pure sodium containing solutions are used (Fig. 7). Apparently, the insertion of a large amount of Li^+ into the lattice opens more sites to sodium ion exchange. In these experiments the ratio of solution to solid exchanger was variable and adjusted to allow a large build-up of exchanged ions.

Discussion

Tsuji and Abe (2, 8) have examined the ion exchange behavior of a hydrous manganese dioxide prepared by oxidation of Mn(II) by KMnO_4 . The product was assigned the formula $\text{MnO}_2 \cdot 0.28\text{H}_2\text{O}$ with a small amount of potassium ion as impurity. From its X-ray powder pattern and thermal behavior it was assigned the cryptomelane or $\alpha\text{-MnO}_2$ structure. In the ion exchanged form the solid may be considered a member of the hollandite family (16) of general formula $\text{A}_{2x}\text{Mn}_{8-x}^{\text{IV}}\text{Mn}_x^{\text{II}}\text{O}_{16}$ where $0 \leq x \leq 1$.

With this formula the exchange capacity for K^+ should be 2.87 meq/g. The observed value was ≈ 2 meq/g.

Our electrolytically prepared manganese dioxide, although amorphous, was certainly not of the cryptomelane type. Its ion exchange capacity was roughly double that expected for cryptomelane, it exhibited different selectivities and it did not contain Mn(II). After exchanging with Li^+ and heating to above 500°C the solid is converted to the lithium spinel LiMn_2O_4 .

Thackeray *et al.* (5, 6) have shown that Li^+ can be inserted into MnO_2 whereas we have accomplished the same result by ion exchange followed by heating. A similar exchange reaction did not occur with the EMDO prepared at 95°C , indicating a lack of hydrogen ion in this solid. Thackeray *et al.* (15) also demonstrated that the lithium ion can be removed from LiMn_2O_4 electrochemically, and that a continuous solid solution of the type $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ exists. The lower limit of composition was $\text{Li}_{0.25}\text{Mn}_2\text{O}_4$. In this case the decreasing lithium ion content was compensated by oxidation of Mn(III) to Mn(IV). However, Hunter showed that Li^+ could be completely removed from the spinel by washing it with acid to yield a so called $\lambda\text{-MnO}_2$ (20). He

explained this transformation on the basis of a surface reaction to remove Li^+ followed by disproportionation of the Mn^{3+} to soluble Mn^{2+} and insoluble Mn(IV) . We believe that the acid treatment merely results in exchange of H^+ for Li^+ since our spectral and thermal analysis is in agreement with the formula HMn_2O_4 and the compound exchanges Li^+ for H^+ completely. In addition less than 1% of the manganese dissolved on treatment with acid. Hunter dried his acid treated solid at 95°C and this removes most of the water making it appear as though only MnO_2 was the product.

We prepared our lithium spinel by heating either the Li^+ exchanged EMDOs or a mixture of $\text{Li}_2\text{CO}_3 + \text{MnO}_2$ at 520°C for 4–10 hr. The product was poorly crystallized as shown by the broadness of the X-ray reflections. Thus, the counterdiffusion of H^+ and Li^+ may be facilitated by the many defects in the lattice resulting from incomplete crystallization. The spinels prepared at correspondingly higher temperatures did not exchange as readily, and in agreement with the observations of Hunter (20) and Thackeray (15), not all the Li^+ was removed. However, up to 4% Mn^{2+} dissolved in our acid treatment of these spinels; but the ion exchange reaction could still be carried out, albeit with lower total lithium ion removal. Thus, we conclude that a proton containing spinel formed in these cases also and not $\gamma\text{-MnO}_2$. Treatment with stronger acid for longer periods of time resulted in increased solubility of manganese.

It is the narrow passageways to the tetrahedral sites which give the spinel its high selectivity for Li^+ . The small amounts of Na^+ and K^+ which are exchanged from pure solutions of these ions are probably due to surface exchange. In the presence of Li^+ however, about twice the original capacity of sodium ion was taken up. Apparently the imperfect spinel lattice formed at 500°C is able to expand sufficiently to allow more Na^+ to diffuse into the interior.

In contrast to the lithium specific spinel a comparable sodium ion phase was not obtained. Rather, layered phases related to those reported in the literature were obtained (17, 18). While the X-ray patterns of the hydrated phases agree with those of Giovanoli (17, 19), their compositions do not. For example, we have represented the hydrogen ion phase as $\text{H}_4\text{Mn}_9\text{O}_{18}$. If the manganese valence does not change on acid treatment of the sodium phase then it should have the formula $\text{Na}_4\text{Mn}_9\text{O}_{18}$, that is $\text{Na}_{0.44}\text{MnO}_2$. However, the phase of this composition reported by Parant *et al.* (18) yields a totally different X-ray pattern. Furthermore $\text{Na}_{0.44}\text{MnO}_2$ has a tunnel structure and not a layered one.

Another possibility is that the original sodium ion phase formed at 500°C is a variant of one of the $\text{Na}_{0.7}\text{MnO}_{2+y}$ phases. Its X-ray powder pattern (only two reflections at 5.54 and 2.76 Å) matches those reported for the α - and β -forms of $\text{Na}_{0.7}\text{MnO}_{2+y}$ and these phases are layered. However, its sodium content is too low. Hirano *et al.* (21) prepared $\text{Na}_{0.7}\text{MnO}_2$ by a hydrothermal method in strong NaOH . They showed that washing in water removed some of the sodium and introduced hydronium ions in their place. In the process the layers swelled from 5.64 to 7.19 Å. This behavior resembles that of our sodium containing phase, but on total removal of Na^+ with acid, the replaceable protons should number 0.7 per Mn. This should yield an ion exchange capacity of about 6 meq/g, considerably more than observed. Thus the entire question of the sodium ion phases needs further study.

Layered compounds which can readily expand the interlayer distances to accommodate ions of different sizes tend not to show high specificity in their ion exchange behavior. However, phases with tunnel structures, pyrochlores, and other tightly spaced lattices like spinels may do so. An exploration of such possibilities and of fur-

ther relationships with insertion reactions is in progress.

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