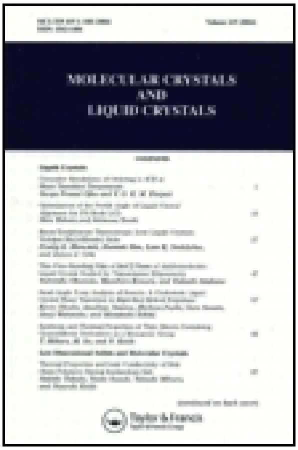

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The 2D Rancieite-type manganic acid and its Li-exchanged derivative: A new synthetic route for a better cycling behavior

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The 2D Rancieite-type manganic acid and its Li-exchanged derivative: a new synthetic route for a better cycling behavior.

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The usual preparation route of lithiated Rancieite-type Manganese Oxide (Li-RMO) includes three steps: reduction of $KMnO_4$ in acidic medium (1), followed by a further acidic treatment which ensures a complete K^+/H^+ exchange (2) and subsequent Li^+/H^+ ion-exchange reaction (3). The surface area of the as prepared Li-RMO is always several tens of m^2g^{-1}. Its initial capacity with respect to electrochemical Li intercalation is 220 mAh/g with an average voltage of 2.85V (vs Li). However, a rapid capacity fading is observed upon cycling, due to a dissolution of the material likely related to its large surface area. A new synthetic route is proposed leading to a material with a surface area less than 10 m^2g^{-1}. As expected, the cycling behavior of this new material is greatly improved.

Keywords: phyllomanganate; surface area; Li intercalation; cycling behavior

INTRODUCTION

The 2D Rancieite-type manganic acid and its Li-exchanged derivative (called RMOs: Rancieite Manganese Oxides), prepared from $KMnO_4$ aqueous reduction, have been thoroughly characterized recently[1]. It has been shown that the Li-derivative, annealed at 300°C, exhibits a promising application-oriented behavior as a cathode material for Li batteries, with a large initial capacity of about 220 mAh/g at an average voltage of 2.85V[4]. However, further studies have revealed that the capacity retention upon cycling was clearly insufficient with, in some cases, a prohibitively large capacity loss of ≈2% per cycle [5]. The results of investigations intended to identify the reasons and to find a remedy for this, are reported in this paper.

EXPERIMENTAL

A combination of techniques was used to characterize the materials including X-Ray diffraction (XRD), chemical analyses, thermal analyses, surface area measurements...

XRD patterns were recorded with the use of a Siemens D5000 diffractometer using CuKα radiation. Thermal analyses were made on a Perkin-Elmer TGS-2 TGA system and the surface areas were measured with the use of a Quantasorb Junior equipment by the single point BET technique.

Composite electrodes were prepared by mixing the active material, a carbon black (Super-S from Chemetals Inc., Baltimore, MD, USA) and a binder (polyvinylidene difluoride: PVDF) in a ratio by mass of 85:10:5, respectively, and then coating this mixture onto an aluminium disk serving as the current collector.

Standard laboratory Swagelok™ test cells were used with the composite electrode as the positive and Li metal as the negative, separated by glass paper soaked in electrolyte. The electrolyte was made of 1M $LiPF_6$ dissolved in a 2:1 mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). The cells were tested between 3.8 and 2V using the Mac-Pile system operating in a galvanostatic mode.

RESULTS AND DISCUSSION

Identification of a possible cause of capacity fading

Swagelok test cells containing the 2D prelithiated Rancieite Manganese Oxide annealed at 300°C (300-Li-RMO) as the cathode active material, which had a poor capacity retention upon cycling were dismounted after several tens of cycles and analyses of the electrode materials were made. XRD patterns of the composite cathode materials have features charasteristic of the active material, still poorly crystallized, as expected. On the other hand Mn was easily detected by microprobe analyses of the Li anodes, suggesting a partial dissolution of the cathode active material during the reversible deintercalation process. It has already been mentioned that the surface area of the H-RMO (Rancieite

Manganese Oxide in protonic form) materials can reach 330 m^2g^{-1} [1]; such a large surface area is likely to favor the dissolution of the material. Investigations of the various preparation steps of the active electrode material and their influence on its surface area were therefore undertaken.

Investigations on the various preparation steps of Li derivatives

The usual preparation route of Li-RMO materials, derived from a method already proposed by Tsuji et al.[6], includes three steps: (1) 0.1 dm^3 of 4M HCl are added to 0.6 dm^3 of 1M $KMnO_4$ aqueous solution at 60°C, leading to a precipitate which is washed with distilled water until free from KCl, (2) the as prepared manganic acid (it is called HK-RMO) contains about 10% (per Mn atom) of K^+ ions that can be ion-exchanged with H^+ in 1M HNO_3 leading to an almost K^+ free H-RMO ($Mn^{III}_{0.02}Mn^{IV}_{0.98}O_{1.99}$,$1.3H_2O$), (3) Li-RMO ($Li_{0.42}Mn^{III}_{0.02}Mn^{IV}_{0.98}O_{2.2}$,$1.4H_2O$) is obtained by ion-exchange at room temperature (RT) in a large excess of equimolar solutions of 1M LiCl and 1M LiOH.

It must first be mentioned that in step (1), corresponding to the Mn^{VII} reduction, the reaction is far from being complete, due to an insufficient amount of acid.

Second, this reaction is exothermic and, depending on the rate of addition of acid, the temperature increase can be large. For example, after dropwise addition the temperature reaches ≈100°C and the resultant precipitate is no longer HK-RMO, but the cryptomelane compound $K_2Mn_8O_{16}$. Better control of the reduction temperature (between 60 and 65°C) and a complete reaction were achieved thanks by slow addition of a six times larger quantity of HCl.

This modified first step leads to HK-RMO materials that are highly reproducible in terms of surface area (10-15 m^2g^{-1}), K content (≈10%) and mean oxidation state (MOS) of Mn (≈3.8). These characteristics were again analyzed at the end of the second step leading to H-RMO compounds. As expected only trace amounts of K were detected. Rather surprisingly the MOS of Mn was close to 4. This is a likely consequence of the Mn^{III} disproportionation to Mn^{II} and Mn^{IV}, as suggested by the weight loss of the samples in the course of K^+/H^+ ion-exchange reaction as the Mn^{II} species are soluble. However, the most striking feature of this second step is 10-fold increase in surface area (100-150 m^2g^{-1}); this K^+/H^+ ion-exchange reaction appears to be genuine chemical grinding.

Various attempts to modify the third step were made with the aim, among others, of increasing the Li content. Ion-exchange reactions were made in solution from RT to 80°C, starting from H-RMO materials. The results are the following: (1) an increase of the reaction temperature decreases the ion-exchange duration but does not modify the final Li content, (2) the MOS of Mn remains unchanged but surprisingly the surface area is halved (50-75 m^2g^{-1}); this latter reproducible result is not understood.

At this level of our study, the surface area of the Li derivatives prepared by a three step process (hereafter called (3)Li-RMO) is rather large and their capacity retention in a Li battery is far from satisfactory, as it will be seen later. On account of the importance of the K^+/H^+ ion-exchange step in determining the surface area of the final materials, attemps to avoid this reaction were made:

- by adding a large quantity of LiCl (Li/Mn=10) to the HCl solution used for the Mn^{VII} reduction. Unfortunately the resulting material contained only traces of Li.

- by subjecting the HK-RMO material from the first step to a $(K^+,H^+)/Li^+$ ion-exchange reaction at RT in a large excess of equimolar solutions of 1M LiCl and 1M LiOH (1g of HK-RMO/l). This new two step process leads to a Li derivative (hereafter called (2)Li-RMO ($Li_{0.42}Mn^{III}_{0.2}Mn^{IV}_{0.8}O_{2.11},1.4H_2O$)) whose Li content is similar to that of (3)Li-RMO, with the great advantage of a surface area identical to that of the starting HK-RMO material (≈10 m^2g^{-1}).

Electrochemical studies

The electrochemical behaviors of (3)Li-RMO and (2)Li-RMO with respect to Li intercalation were compared at RT. Prior to the electrochemical studies, the materials were dehydrated at 300°C for two hours. This thermal treatment does not modify the surface areas, but the MOS of Mn decreases slightly from ≈4 to ≈3.94 for (3)Li-RMO and remains nearly the same for the (2)Li-RMO, the water content becoming negligible.

The first discharge curves of two Li-RMO materials ((3)Li-RMO: 50 m^2g^{-1} and (2)Li-RMO: 7 m^2g^{-1}) at similar rates (≈C/6) exhibit similar shapes [4]. However the initial capacity of (2)Li-RMO is smaller than that of (3)Li-RMO (0.35Li/Mn instead of 0.55). This difference could be related to the difference in grain size of the materials in connection with their surface area. Since the intercalation kinetics are the same, the reaction takes longer when the grain size is larger. Despite this difference, the capacity retention upon cycling at similar intercalation-deintercalation rates was investigated for these materials. The evolution of their specific capacities over the first 50 cycles is represented in fig. 1 which shows an almost linear capacity decrease for (3)Li-RMO whereas (2)Li-RMO retains its initial capacity at a given rate. The capacity decrease observed upon changing from C/12 to C/6 (for (2)Li-RMO) illustrates the kinetics limitation mentioned above.

An even more clear relationship between the surface area of the Li-RMO and their capacity retention is illustrated in fig. 2 where the cycling behaviors of three different materials are compared. The average capacity decrease over the first 50 cycles is ≈1.4%/cycle for sample S1 (surf. area 83 m^2g^{-1}), ≈0.6%/cycle for S2 (surf. area 50 m^2g^{-1}), and negligible for S3 (surf. area 7 m^2g^{-1}).

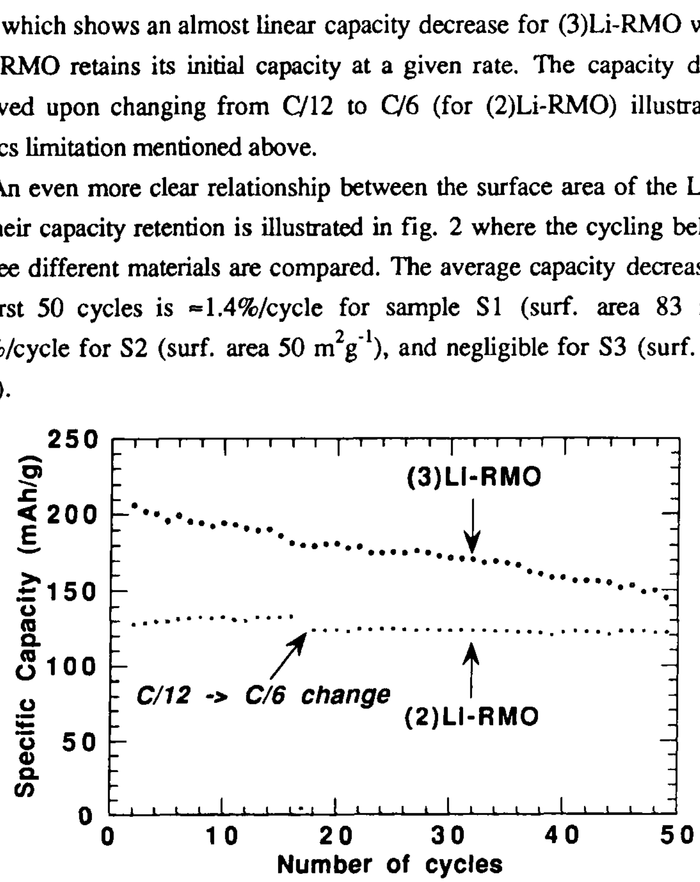

FIGURE 1 Evolution of the specific capacity of two Li-RMO samples over the first 50 cycles.

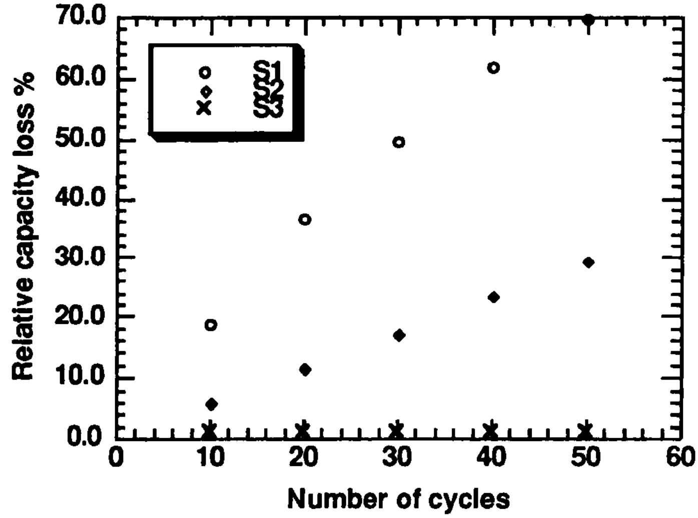

FIGURE 2 Evolution of the relative capacity loss over the first 50 cycles for three Li-RMO samples with different surface areas.

CONCLUSION

The rapid capacity fading of Li-RMO materials upon cycling is due to their dissolution, likely favored by their large surface area. A new synthetic route is proposed leading to Li-RMO materials with a surface area ≤10 m^2g^{-1}. The cycling behavior of such materials is dramatically improved and the capacity loss over the first 50 cycles is negligible.

References

[1.] F. Leroux, D. Guyomard and Y. Piffard, *Solid State Ionics*, **80**, 299, (1995).
[2.] O. Glemser, G. Gattow and H. Meisiek, *Z. Anorg. Allg. Chem.*, **309**, 1, (1961).
[3.] G. Sterr and A. Schmier, *Z. Anorg. Allg. Chem.*, **368**, 225, (1969).
[4.] F. Leroux, D. Guyomard and Y. Piffard, *Solid State Ionics*, **80**, 307, (1995).
[5.] F. Leroux, *Ph D Thesis*, (Nantes, FRANCE) (1995).
[6.] M. Tsuji, S. Komarneni, Y. Tamaura and M. Abe, *Mat. Res. Bull.* **27**, 741, (1992).