



Reversibility of lithium intercalation in lithium and sodium phyllosulfates

F. Le Cras, S. Rohs, M. Anne, P. Strobel *

Laboratoire de Cristallographie, CNRS, BP 166, 38042 Grenoble Cedex 9, France

Abstract

The cycling of sodium and lithium phyllosulfates in liquid lithium batteries was investigated both by galvanostatical and potentiostatical methods. Slow-scanning voltammograms show the occurrence of a single-phase reaction extending from 3.1 to 2.6 V on discharge for both compounds. On cycling, the voltammogram of Li phyllosulfate smears out, while the current peak narrows in the case of Na. In both cases, the initial capacity of ~ 240 Ah/kg drops continuously on cycling between 2 and 4 V. X-ray diffraction shows an important disordering with cycling, with the possible emergence of a cubic-packed, spinel-like structure.

Keywords: Lithium intercalation; Phyllosulfates; Sodium

1. Introduction

The intercalation of lithium in manganese-containing oxides for battery applications has been the subject of intense research [1]. But most manganese oxide compounds considered do not actually have an open structure, as found in TiS_2 or even V_2O_5 . Pyrolusite and ramsdellite (as well as $\gamma\text{-MnO}_2$) have one-dimensional tunnels, which are ineffective for reversible intercalation [2,3]. The spinel structure of LiMn_2O_4 has tunnels interconnected in three dimensions, and has better intercalation/de-intercalation properties. However, it displays two well-separated voltage plateaus versus Li, one around 3 V, corresponding to a two-phase transition between a cubic and a tetragonal, Jahn–Teller distorted phase, and the other above 4 V, which raises problems of electrochemical stability towards other battery components.

We reported recently the characteristics of lithium intercalation into layered manganates, or phyllosulfates [4,5]. Their structure (also referred to after the mineral birnessite) is the most open structure known for manganese oxidic compounds. It is built-up of CdI_2 -like MnO_2 sheets separated by open interlayer spaces containing other cations A and water molecules. The chemical formula can be written as $\text{A}_x\text{MnO}_{2\pm\delta}\cdot z\text{H}_2\text{O}$,

where δ reflects the presence of manganese vacancies in the MnO_{-2} layers. These compounds are best synthesized by low temperature, ‘soft chemistry’ techniques in alkaline aqueous media [6], resulting in the incorporation of alkali cations and water in the structure.

The interlayer species are loosely bound and cation exchange can be readily carried out in phyllosulfates. The weak bonding between layers also results in stacking disorder from one layer to the next, hence in usually poorly resolved X-ray diffraction patterns, except for the prominent (001) reflections. Three further points must be pointed out here:

(i) Li phyllosulfate cannot be made directly. Moreover, the direct ion exchange Na^+ (or K^+) \rightleftharpoons Li^+ is ineffective. We succeeded in preparing Li phyllosulfate by a two-step route described below.

(ii) The openness and the disorder allowed in this structure should make the reversible cycling down to the ‘Jahn–Teller range’ of manganese (i.e., below the average oxidation state 3.5+) easier than in rigid frameworks such as the spinel structure.

(iii) Using a combination of thermogravimetry and X-ray measurements under vacuum, we showed that the structure remains stable in the absence of interlayer water molecules [7].

Drying phyllosulfates results in a decrease of the interlayer space (related to the c -parameter of the hexagonal subcell), which is governed by the size of

* Corresponding author.

the A cation in the anhydrous phases [4]. We believe the removal of water is likely to have implications on the reversibility of lithium intercalation. However, fairly large capacities were reported in phyllo-manganates prepared by sol-gel techniques and used in lithium cells without dehydration [8].

In our previous work [5], we found that the nature of the counter-cation A had little influence on the discharge behaviour of $A_x\text{MnO}_{2\pm\delta}$ compounds, but the data reported did not exceed three cycles and did not include Li phyllo-manganate. This paper presents our recent results focusing mainly on cycleability and the use of a new Li phyllo-manganate.

2. Experimental

The synthesis of Na phyllo-manganate was described previously [6]. Li phyllo-manganate was prepared as follows. Firstly, a suspension of Na phyllo-manganate was stirred in 0.5 M nitric acid for 8 h at 20 °C, filtered and washed. This gives an alkali-cation-free phyllo-manganate, with formula close to $\text{Mn}_8\text{O}_{15}\cdot 6\text{H}_2\text{O}$. The latter compound was then stirred in 1 M LiOH for 24 h at low temperature. The filtered product was dried at 80 °C.

All the compounds obtained by these low-temperature techniques are finely divided, submicronic powders with a lamellar habit. Their X-ray diffraction patterns (see Fig. 6) show 2θ values (Cu $K\alpha$ radiation) ≈ 12.5 , 25 and 37°, respectively, corresponding to the (001), (002) and (110) reflections of the classical hexagonal subcell common to the phyllo-manganate family.

Compositions determined from chemical analysis are given in Table 1. The average oxidation state of Mn in Na phyllo-manganate is close to 3.5. We recently succeeded in increasing significantly the manganese oxidation state in Li phyllo-manganate (compare samples Li-17c and Li-SR11 in Table 1). These compounds have theoretical capacities for lithium insertion close to 300 Ah/kg, considering the Mn^{4+} – Mn^{3+} redox range (see Table 1). In addition, preliminary tests showed that,

unlike manganese spinels, these compounds have a smooth, stepless discharge curve throughout this whole range, corresponding to voltages from about 3.6 to about 2 V versus Li/Li^+ [5].

Cathodes were made of intimate mixtures of the oxides with 20% acetylene black and 10% polytetrafluoroethylene, pelletized and vacuum-dehydrated at least 48 h in an argon glove box antechamber before use. The electrolyte was a 1 M solution of LiClO_4 in dried propylene carbonate–ethylene carbonate–dimethoxyethane (1:1:2). Lithium perchlorate was dried at 160 °C in vacuum for 60 h before use. The anode was made of freshly scraped lithium foil. Button-type cells CR2430 were filled and sealed in a glove box with less than 1 ppm H_2O . Cells with typically capacities ~ 10 mAh were controlled either potentiostatically for very slow-scanning voltammetry (typically 10–30 mV/h), or galvanostatically with currents $\leq 50 \mu\text{A}/\text{cm}^2$, using a 16-channel MacPile controller (Biologic Co., Claix, France).

3. Results and discussion

3.1. Discharge characteristics

The first discharge/charge cycle of Li and Na phyllo-manganate cells (Fig. 1) shows that the whole redox process takes place along a continuous voltage decrease without marked plateau. The corresponding voltammograms (Fig. 2) exhibit single, wide peaks occurring in the range 3.1–2.6 V on discharge, 2.9–3.4 V on charge. The overlap between discharge and charge peaks in voltammograms shows that the charge/discharge mechanism does not proceed via a two-phase reaction, as is the case for the spinel system LiMn_2O_4 – $\text{Li}_2\text{Mn}_2\text{O}_4$. The shape of the discharge curves is rather similar for sodium and lithium compounds. However, the discharge peak voltage of Li phyllo-manganate (≈ 2.70 V) is slightly, but significantly lower than that of its sodium homologue

Table 1
Characterization and theoretical capacity of layered and spinel-type manganese oxides

Sample	Structure	Experimental composition	Mn oxidation state	Molar mass per Mn	Δx max. per Mn	Theoretical capacity (Ah/kg)
Na-17	hex ^a	$\text{Na}_{0.19}\text{MnO}_{1.83}$	3.48	88.65	1	302
Li-17c	hex ^a	$\text{Li}_{0.25}\text{MnO}_{1.90}$	3.56	87.14	1	307
Li-SR11	hex ^a	$\text{Li}_{0.29}\text{MnO}_{2.08}$	3.86	90.17	1	297
Spinel	cub ^b	LiMn_2O_4	3.50	90.41	(3V: 0.5) (4 V: 0.5)	148 148

^a hex = hexagonal.

^b cub = cubic.

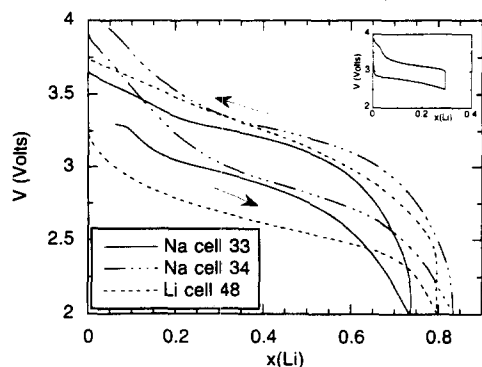


Fig. 1. First potentiostatic discharge/charge curve of Li and Na phyllomanganates at 10 mV/h (Inset: same data for LiMn_2O_4 .)

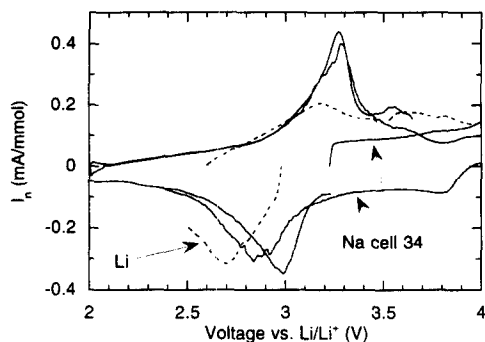


Fig. 2. First cycle voltammograms of Li and Na phyllomanganates at 10 mV/h.

(2.85–3.0 V). In addition, the lithium phase gives a much less well-defined oxidation peak on recharge, indicating structural changes in the material on cycling.

A comparison with the spinel system (see Fig. 1, inset) shows several important differences:

(i) As noted above, the intercalation/de-intercalation reaction in spinel occurs on a voltage plateau (almost flat at 10 mV/h), corresponding to a two-phase reaction. No such marked plateau exists for phyllomanganates.

(ii) The initial capacity $x(\text{Li})$ is much higher in phyllomanganates than in LiMn_2O_4 . The first cycle of cell 34 (Na phyllomanganate) in the range 2–4 V gives $\Delta x = 0.82$, i.e., close to the theoretical, 300 Ah/kg capacity.

Since the oxidation state of manganese is lower than 4+ in the starting material (Table 1), the cycling can begin with a charge. This is valid not only for a lithium de-intercalation, but also for Na phyllomanganate. An example is shown by cell 34 in Fig. 2, where the initial charge corresponds quantitatively to oxidation into Mn^{4+} . This means that sodium can be de-intercalated from the cathode in a lithium cell. This initial sodium removal did not result in any detrimental effect to the cell performance. (Note that a Li/Na cell using Na phyllomanganate, sodium perchlorate and a lithium anode was recently described by Bach et al. [9].)

The effect of varying the discharge regime can be seen in Fig. 3. The capacity is not significantly altered

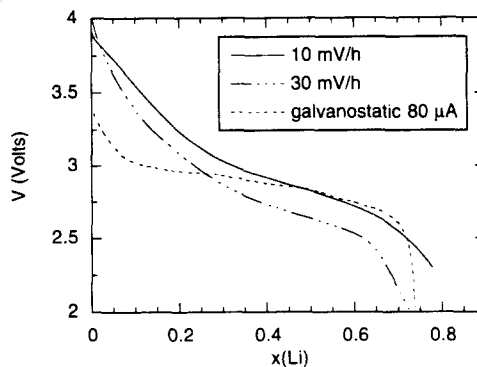


Fig. 3. Influence of the discharge regime on the discharge curve for Na phyllomanganate. The curves correspond to $C/200$ (10 mV/h), $C/70$ (30 mV/h), and $C/90$ (80 μA).

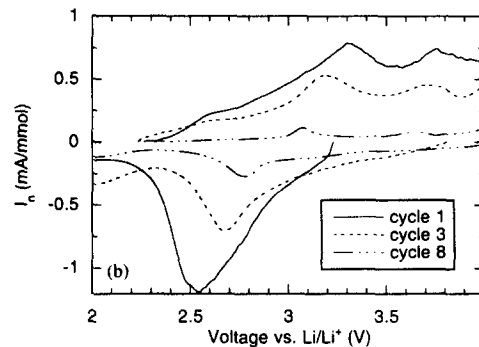
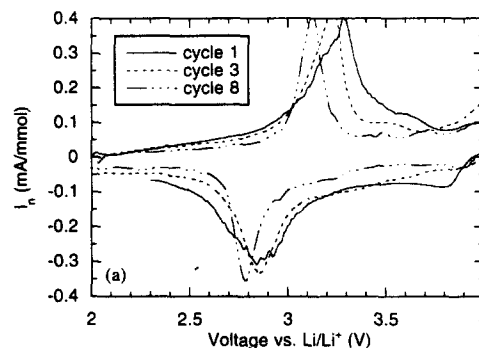


Fig. 4. Comparison of 1st, 3rd and 8th cycle voltammograms for (a) Na phyllomanganate, and (b) Li phyllomanganate.

by the discharge regime in the range studied ($\leq C/60$), showing that the rates used are slow enough to yield near-equilibrium data. Higher cycling rates could not be used reliably because of dendrite formation at the lithium electrode on charge.

3.2. Cycling and reversibility

The evolution of voltammograms with cycling can be seen in Fig. 4. For Na phyllomanganate, the redox peaks are progressively shifted towards lower potentials and get rather narrower. The opposite is observed with the lithium compound (Fig. 4(b)), where the current peaks flatten until reaching an almost featureless voltammogram after 6 to 8 cycles. Accordingly, the capacity

of Li phyllomanganate is always lower than that of its sodium homologue (see Fig. 5). In fact, a constant decrease is observed in both cases, but the Na phyllomanganate retains 150 Ah/kg after 8 to 10 cycles.

X-ray diffraction shows that both compounds are considerably amorphized by cycling (Fig. 6). This is not necessarily a drawback for lithium exchange. But X-ray diagrams after cycling also show the emergence of a broad peak around $2\theta(\text{Cu})=18^\circ$, which could be due to the progressive formation of an oxygen cubic packing such as that of the spinel structure. In any case, it seems that cycling through the Jahn–Teller region ($\text{Mn}^{3.5+}-\text{Mn}^{3+}$) considerably alters the structure and represents as much of an obstacle as in the spinel case [10], although these disordered materials do not

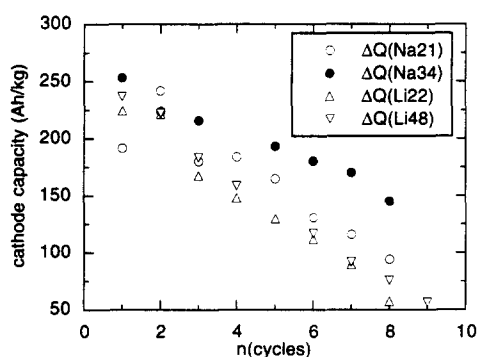


Fig. 5. Evolution of the cell capacity with the number of cycles (potentiostatic mode, 10–30 mV/h).

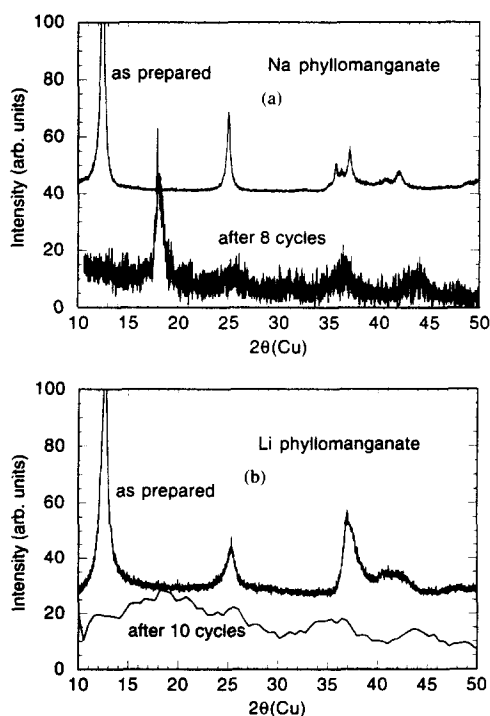


Fig. 6. Effect of cycling on the powder X-ray diagrams of (a) Na phyllomanganate, and (b) Li phyllomanganate.

exhibit two separate reduction processes from Mn^{4+} to Mn^{3+} as in the $\lambda\text{-MnO}_2\text{-LiMn}_2\text{O}_4\text{-Li}_2\text{Mn}_2\text{O}_4$ series.

For Li phyllomanganate, the difficulty of synthesis, the rapid smearing out of the voltammogram, and the collapse of the diffraction lines all confirm the instability of this phase when compared with Na phyllomanganate. This is consistent with ion-size considerations. Lithium is a much smaller ion than sodium. The latter is confined to interlayer sites in phyllomanganates, while lithium can fit in manganese sites, removing any structural stability to the layered phyllomanganate structure.

4. Conclusions

The study of Na and Li phyllomanganates as cathodes for lithium batteries showed that these compounds undergo a single-phase electrochemical redox reaction throughout the entire potential range from 2 to 4 V, without marked difference as a function of the counter-cation (Na or Li). In spite of a high initial specific capacity (~ 250 Ah/kg), the capacity drops continuously with cycling. This drop is accompanied by a rapid disordering of the structure, probably related to the Jahn–Teller effect in the $\text{Mn}^{3.5+}-\text{Mn}^{3+}$ reduction region.

Acknowledgements

This work is part of a research programme in collaboration with CEREM/CEA, Grenoble, and we thank G. Lonchampt and D. Bloch for fruitful discussions. We thank P. Amiot (CRTBT, Grenoble) and C. Disant for their help in chemical analyses. F. Le Cras is funded by a BDCI grant partly supplied by Bolloré Technologies.

References

- [1] J. DeSilvestro and C. Haas, *J. Electrochem. Soc.*, **137** (1990) 5C.
- [2] M.M. Thackeray, M.H. Rossouw, R.J. Gummow, D.C. Liles, K. Pearce, A. De Kock, W.I.F. David and S. Hull, *Electrochim. Acta*, **38** (1993) 1259.
- [3] B. Zachau-Christensen, K. West, T. Jacobsen and S. Skaarup, *Solid State Ionics Conf., The Hague, Netherlands, 1993*.
- [4] P. Strobel, *Mater. Res. Symp. Proc.*, Vol. 293, Materials Research Society, Pittsburgh, PA, USA, 1993, p. 63.
- [5] P. Strobel and C. Mouget, *Mater. Res. Bull.*, **28** (1993) 93.
- [6] P. Strobel, J.C. Charenton and M. Lenglet, *Rev. Chim. Miner.*, **24** (1987) 199.
- [7] J.C. Charenton and P. Strobel, *Solid State Ionics*, **24** (1987) 333.
- [8] S. Bach, J.P. Pereira-Ramos, N. Baffier and R. Messina, *Electrochim. Acta*, **36** (1991) 1595.
- [9] S. Bach, J.P. Pereira-Ramos and N. Baffier, *Electrochim. Acta*, **38** (1993) 1695.
- [10] M.M. Thackeray, M.H. Rossouw, A. De Kock, A. De La Harpe, R.J. Gummow, K. Pearce and D. Liles, *J. Power Sources*, **43/44** (1993) 289.