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Electroactivity of natural and synthetic triphylite

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Abstract

The electrochemical behavior of three triphylite (LiFePO₄) ores from different mining localities has been investigated. Two of them show clearly an activity corresponding to the triphylite phase. A discharge capacity of 85 mAh g⁻¹ was obtained. The benefit of heat treatment that allows to deposit the electronically conductive carbon-based coating on the particles is reported for both natural and synthetic LiFePO₄ samples. Discharge capacity, kinetics and stability upon cycling were all improved after the heating process. The best results were obtained with carbon coatings coming from the decomposition of a modified polycyclic aromatic. In this case, for synthetic samples, the whole capacity was reversibly exchanged and less than 1% of the initial capacity was lost after 10 cycles. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Recently, Padhi et al. [1,2] suggested the use, as cathode for lithium battery, of a new compound having the olivine structure: LiFePO₄. This iron-based compound is environmentally benign and inexpensive. Insertion of lithium occurs reversibly with a very flat discharge plateau at about 3.4 V versus Li⁺:Li⁰. LiFePO₄ and delithiated FePO₄ though not intermiscible belong to the same space group with only small changes in the unit cell parameters. Both LiFePO₄ and FePO₄ structures remain unchanged up to 400°C. The preservation of the main features of the crystal structure makes the material stable upon cycling with no temperature limitations. Unfortunately, the accessibility of 0.6 Li atoms per formula unit of LiFePO₄ found by these authors limits the practical capacity to 100–110 mAh g⁻¹, from the theoretical one (170 mAh g⁻¹).

The promises carried by this early work induced studies aimed at an increase of the reversible capacity and the reaction kinetics. Takahashi et al. [3] and Andersson et al. [4] have shown that the LiFePO₄ capacity was strongly dependent of the cycling temperature. But in both cases, even at 80°C, the theoretical capacity of 170 mAh g⁻¹ was not reached. In a previous work [5] we set up a synthesis

leading directly to carbon-coated particles. We showed that the theoretical capacity of LiFePO₄ could be obtained with this electronically conductive sample. In this case the kinetics were also enhanced.

It is both appealing and attractive to think that this promising cathode material is a well known mineral, available in nature, neither scarce nor expensive and that its electrochemical behavior has never been studied (to the best of our knowledge).

In the present paper, we report some electrochemical characterizations of natural triphylite samples from different mining locations and a comparison with a non carboneous synthetic one. The benefit of a thermal cure leading to carbon-coated, therefore, electronically conductive triphylite particles was investigated for both natural and synthetic materials.

2. Natural triphylite

Natural triphylite Li(Fe, Mn)PO₄ usually forming bluish or grayish, glassy masses, occurs in complex granitic pegmatite dykes. It is within the solid solution series ranging from the similar, but more brightly colored (brown, yellow, or salmon) lithiophilite LiMn_{1-x}Fe_xPO₄ which differs from triphylite by being on the manganese-rich side versus iron; i.e. a continuous chemical variation exists in nature between the pure iron compound and the pure manganese compound.

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Table 1
Chemical analysis of natural and synthetic triphylite^a

Sample	Fe (%)	Mn (%)	Li (%)	K (%)	Ca (%)	P (%)	Maximum purity (%)
Maine	20.2	4.9	3.6	1.1		14.6	71
Dakota	21.1	7.6	2.0	1.7	1.6	15.2	45
Palermo	20.6	5.2	3.6	1.3		14.6	73
Synthetic	34.5		3.7			18.8	84

^a Data were obtained by ICP.

The structures of the two minerals are the same and therefore any differences in physical properties between the two would be related to the iron/manganese ratio. In order to investigate the influence of this ratio on the electrochemical behavior of triphylite, three samples from different mining localities (Palermo Mine North Gorton, NH; Lord's hill, Maine; Custer, SD) were purchased from Excalibur Mineral Company. Well-defined triphylite crystals are quite rare. More commonly triphylite occurs as compact cleavable masses with intergrown crystal clumps. The surfaces exposed at room atmosphere are weathered and may contain the delithiated material FePO_4 .

3. Experimental

Triphylite ores were ground as received in a ball mill in deoxygenated isopropanol. After grinding, powders were dried and stored under inert atmosphere prior to use.

Classical synthetic triphylite was prepared in house. This new process leading to non conductive samples is not yet fully optimized and the obtained materials are not perfectly stoichiometric.

Chemical analyses were made by ICP to determine the stoichiometry and the phase purity of materials were checked by X-ray diffraction.

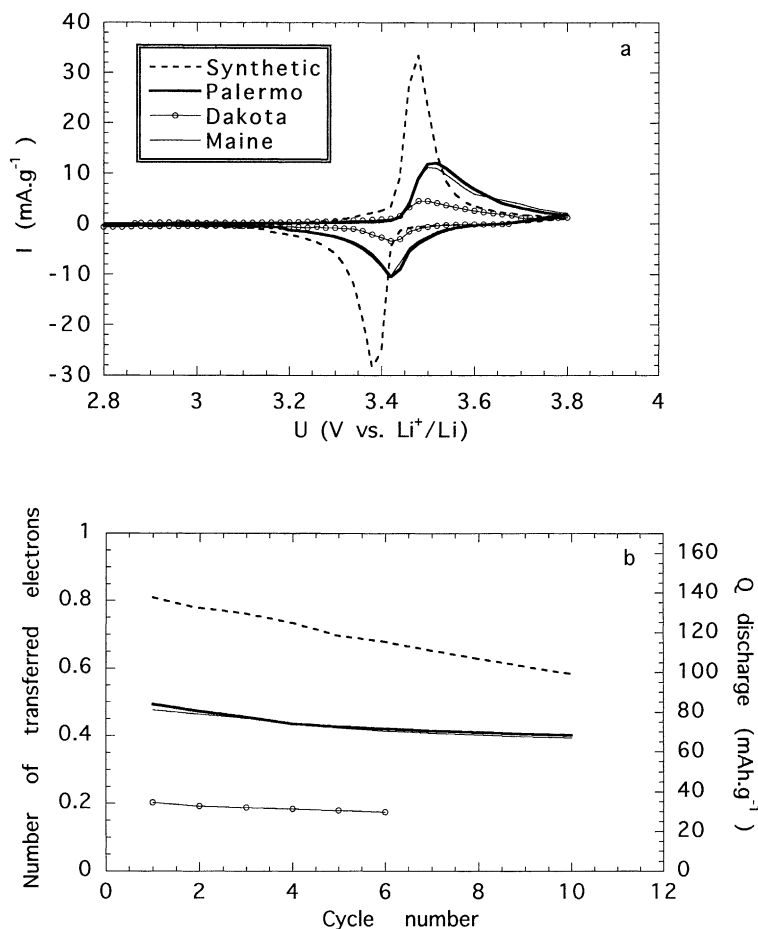


Fig. 1. First voltammetric scans (a); evolution of the discharge capacity upon cycling (b) for natural and synthetic triphylite samples. Results obtained by cyclic voltammetry (scan rate 20 mV h^{-1} ; temperature 80°C ; electrolyte PEO-Li salt O/Li = 20/1).

Electronically conductive coatings were obtained for classical and natural LiFePO_4 , from the decomposition of organic substances. We report here results obtained with sucrose, cellulose acetate and a modified polycyclic. The triphylite powder was mixed with a solution of the above carbon precursors (thereafter named organic substances). The dry additive corresponds to 5% of the triphylite weight. After drying, blends are submitted to heat treatment at 700°C under argon atmosphere for 4 h. The quantity of carbon-coated represents about 1% in weight of the material.

The electrochemical investigations were made in lithium batteries with a poly(ethylene oxide) (PEO) bis-trifluoromethanesulfonimide lithium salt (LiTFSI) as electrolyte with a ratio O/Li of 20. Composite cathodes were made of electroactive material, ketjen black, PEO in the proportions 33.8; 9.5; 56.7 by weight, acetonitrile was added to dissolve the PEO. These components were intimately mixed together and spread on a stainless steel current collector (1.7 cm^2). Investigations were performed at 80°C .

4. Results and discussion

Different color powders results of ores grinding. The sample from Maine is beige, the one from Palermo is gray and an intense blue-green color was observed for the powder originating from Dakota. The synthetic material is very pale green.

The shape of the three natural powders was observed by scanning electronic microscopy. In all cases, it contains small micro-particles and some huge massive grains having escaped the grinding process, with sizes up to $50\text{ }\mu\text{m}$.

Unfortunately, the triphylite content of ores was unknown.

The chemical composition of the investigated materials is summarized in Table 1. The detection limit of elements corresponds to 1% by weight of the solid. The maximal purity given in the Table 1 was calculated considering that only the triphylite phase contains the element which presents the highest departure from the stoichiometry (lithium for synthetic and Dakota triphylite, iron and manganese for Maine and Palermo samples). This is a maximum purity

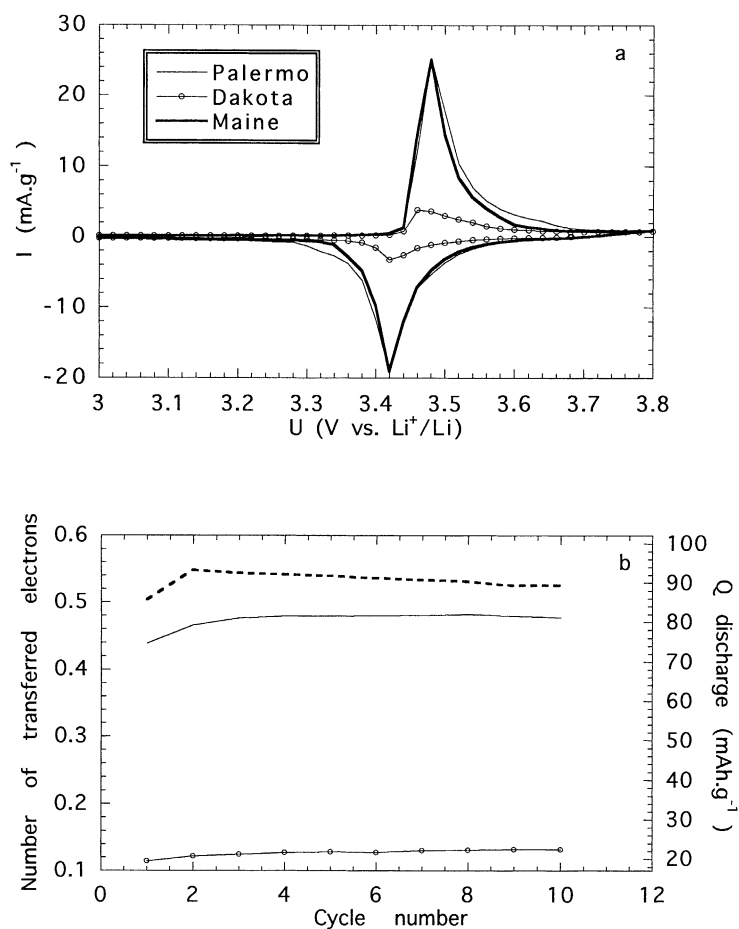


Fig. 2. Tenth voltammetric scans (a); evolution of the discharge capacity upon cycling (b) for carbon-coated natural and synthetic triphylite samples. Results obtained by cyclic voltammetry (scan rate 20 mV h^{-1} ; temperature 80°C ; electrolyte PEO–Li salt O/Li = 20/1).

because it is obvious, in the case of Palermo and Maine samples that iron is involved in other compounds like iron oxides, pyrite, etc. Samples from Maine and Palermo are quite similar in term of purity and manganese content. The X-ray patterns obtained for these samples show that the principal phase is triphylite.

The chemical composition obtained for the Dakota ore is quite disappointing and the X-ray analysis confirmed that this sample was principally not triphylite.

4.1. Electrochemical measurements

First voltammetric scans (Mac Pile, Claix, France) performed at 20 mV h^{-1} on the untreated samples are presented Fig. 1a and the capacities exchanged upon cycling are shown Fig. 1b.

The three natural samples show the oxidation and reduction peak characteristic of triphylite material. An interesting feature of these natural samples versus the synthetic one, is that electrochemical processes are shifted anodically. This is probably due to the presence of the small amounts of manganese. For the Maine sample, electrochemical investigations were also made using a liquid electrolyte up to

4.5 V but no additional electrochemical activity corresponding to the $\text{Mn}^{2+}/\text{Mn}^{3+}$ couple was observed. As expected the Dakota sample shows only a small electrochemical activity corresponding to 20% of the theoretical value. The voltammogram shapes of Palermo and Maine samples are similar and for both almost 50% of the theoretical capacity is reached. Taking into account that the maximal purity of these samples is 70%, the LiFePO_4 phase activity is about 70% in both Palermo and Maine ores. Upon cycling we observe for the later samples, a fade of the electrochemical activity and after 10 cycles, 20% of the initial capacity was lost. The same behavior was also observed for the synthetic sample. In this case only 70% of the initial capacity is retained after 10 cycles.

4.2. Influence of carbon coatings on the electrochemical behavior of natural samples

For natural samples, coatings were obtained by carbonization of modified polycyclic aromatic. The electrochemical behavior of these materials is shown Fig. 2. We reported here the 10th voltammetric scan because carbon-coated samples undergo an activation process during the first cycles

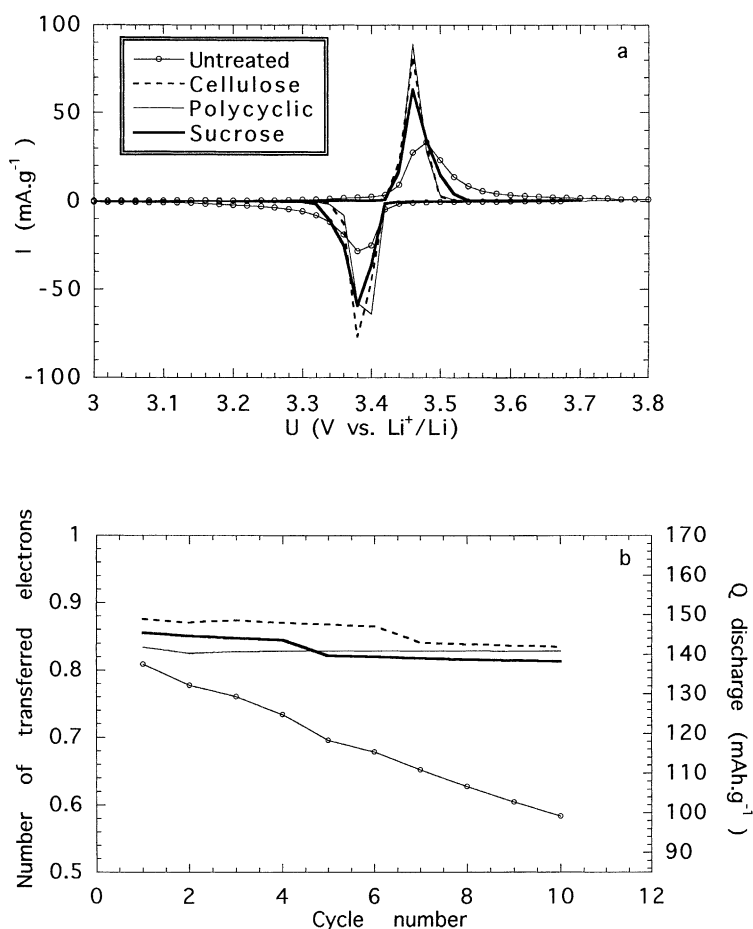


Fig. 3. Tenth voltammetric scans (a); evolution of the discharge capacity upon cycling (b) for carbon-coated synthetic triphylite samples. Results obtained by cyclic voltammetry (scan rate 20 mV h^{-1} ; temperature 80°C ; electrolyte PEO-Li salt O/Li = 20/1).

(Fig. 2a). For the Dakota sample, no improvement due to the coating is visible. As seen before, the shape of Palermo and Maine samples are very similar. Peaks appears to be sharper than for untreated samples while the peak current density in the reduction process is twice higher. Oxidation and reduction processes occurs within a narrower potential range. These later observations indicate an increase in the reaction kinetics. The capacities exchanged are slightly higher but the real improvement is seen with the stability of exchanged charge upon cycling (Fig. 2b). For the Palermo sample, the highest capacity (54.8%) is reached during the 2nd cycle and after 10 cycles, 96% of this initial capacity is retained.

We have to point out that no real improvement in term of capacity due to the carbon coating was observed. The best results were obtained with Palermo sample with a capacity of 54.8%. This capacity could be limited by the purity of the ore that could be inferior to 70%. Actually X-ray diffraction cannot detect impurities in quantity smaller than 5%. These ores contain probably a lot of different compounds. The other and most likely cause of capacity limitation comes from the large particles. Grinding have to be optimized in order to reduce the particles size.

4.3. Influence of the carbon sources

For the synthetic material, carbon coatings were obtained from the decomposition of three different substances. The benefit of these treatments on the kinetics appears clearly in Fig. 3. For the untreated sample oxidation and reduction processes trail over a wide potential range. After coating, peaks get sharper and reduction occurs within a 100 mV range in the case of the samples treated with the modified polycyclic hydrocarbon and the cellulose acetate. The sucrose treated sample gave less efficient results seen on the kinetics (Fig. 3a). The reduction capacity varies from 83% (modified polyaromatic) to 87% (cellulose acetate)

which, taking into account the purity of the synthetic sample, represents the whole capacity of this material. The best results concerning the stability upon cycling were obtained for the sample treated with modified polyaromatic. After 10 cycles less than 1% of the initial capacity was lost (Fig. 3b).

5. Conclusion

The well-defined redox activity of double phosphates from various sources corroborates their interest as a new family of “plateau-type” electrodes whose advantages over “sloping-type” materials are worth consideration. Besides, attention should be drawn to the existence of an appreciable redox activity, yet unoptimized, from a natural compound found in relative abundance in nature; the triphylite family represents one of the most abundant lithium ore. Moreover, we show that, carbon-coated electronically conductive particles could be obtained as a post treatment by a simple and inexpensive way. Resulting materials exhibit enhanced capacity, kinetics and stability upon cycling. Again, these findings point towards the chemical sustainability of this environmentally benign compound.

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