

THE NEW APPROACH OF INTERCALATION MATERIAL FOR THE APPLICATION OF RECHARGEABLE LITHIUM BATTERIES

SHI-JIE WEN*, XIAO-TIAN YIN and L. NAZAR

Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1

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A new approach of lithium electrochemical (de)intercalation material has been put forward. This approach requires a two-compound (physically or chemically) composite in which one is a chemically and electrochemically stable and porous (tunnel, cage, layer, etc.) compound such as clay or zeolite, and the other is a chemically and electrochemically stable and metallic compound such as graphite, metal powder or black carbon. Neither does the redox couple in this composite absolutely exist nor does the redox reaction, which is associated with electrochemical charge and discharge processes when this composite is used as an cathodic electrode in a lithium battery cell. In this paper, we show the results of the lithium electrochemical intercalation process in both black carbon-mixed zeolite and clay electrodes. In these solid electrodes, black carbon serves to delocalize (transport) electrons for balancing the charges while zeolite and clay offer the neutrally reversible sites for lithium ions. This approach can hopefully become a guide for the designing of new intercalation material and so will be very important in the application of the lithium rechargeable battery.

INTRODUCTION

An intercalation compound is a host into/from which a guest species may be topotactically and reversibly inserted/extracted over a finite range of solid solution. Moreover, the guest species may be neutral, an electron donor, or an electron acceptor. Of particular interest for secondary-battery electrodes (host) is the case of an electron donor such as lithium metal (guest). During the lithium intercalation (chemical or electrochemical), the redox reaction may occur on the host cation, the host anion, or the guest species [1, 2]. In the first case, this reaction converts the cathodic electrode back and forth between a metallic or semi-metallic metal oxide to a poor electric conducting metal oxide such as a layered A_xMX_2 compound (here A = alkaline metal such as Li or Na; M = a transition metal such as Ni or Co; and X = O, S, etc.). Furthermore, the topotactic insertion/extraction processes may occur by ionic diffusion in a one-dimensional (1D) compound such as in the hexagonal tungsten bronze [3]; in a two dimensional (2D) compound such as in layered TiS_2 [4] and in a three dimensional (3D) compound such as in the close-packed spinel $Li[Mn_2]O_4$ [5].

* All correspondence should be addressed for Mr. Wen to Science and Technology Center, Tufts University, 4 Colby Street, Medford, MA 02155, USA.

In one of our previous papers [6], as initiated by the studying of the hybrid intercalation composite (pure clay and oxide pillared clay) oriented to the application of lithium rechargeable batteries, we have shown the evidence of lithium electrochemical charge and discharge processes for black carbon-mixed clay solid electrode. There is no obvious redox couple in this mixed composite, and there is no redox reaction associated with the battery charge and discharge processes within the working potential range from 0.5 V to 4 V in this cathodic solid electrode that is set as a lithium battery. To explain electrical neutrality during the ion insertion/extraction, we postulated that the clay in this composite is a host that offers only the neutrally reversible lithium sites with its two dimensional layers. While it is the black carbon that is responsible for the electron circulation and transportation, electrons are delocalized within the black carbon when the electrode is in a discharge process and rejected out of the black carbon when in a charge process.

Can this postulation be extended? If it is really true, it means that we can choose judiciously some openly porous hosts without redox couple and also some electronic conducting support compounds. First of all, we have tried to replace clay with zeolite and found, similar to black carbon-mixed clay cathodic electrode, the evidence of lithium electrochemical (de)intercalation in black carbon-mixed zeolite cathodic electrode with an energy density of more than 200 mAh/g and an energy power density of 300 mW/g in a lithium battery. In this paper, we will show both these results on black carbon-mixed clay and zeolite electrodes.

Based on these experimental results, we are now putting forward a new approach for lithium electrochemical (de)intercalation material. This approach requires a two-compound mixed (physically or chemically) composite in which one is a chemically and electrochemically stable and porous (tunnel, cage, layer, etc.) compound such as clay, zeolite, etc. and the other is a chemically and electrochemically stable and metallic compound such as graphite, metal powder or black carbon. In our particular example here, the first compound is zeolite or clay and the second is black carbon.

Although our study is only at the initial stage, and the electrochemical data is not totally completed, and there is some instabilities and ambiguities during the electrochemical charge and discharge processes, the present results are particularly interesting and prospective. In the following, as a comparison, we will show the lithium electrochemical charge and discharge testing for both black carbon-mixed clay and zeolite solid electrodes.

EXPERIMENTAL

Materials

All the details about the clays used in this paper are the same as in our previous paper [6].

The zeolite 5A and 13X were purchased from the Union Carbide Corporation U.S.A.

The black carbon was purchased from AKZO Co Japan (Ketjenblack EC 600JD).

The zeolite was dried in a vacuum at 200°C for three days before being used to prepare the electrode. Clay, and the black carbon were all dried in vacuum at about 150°C for three days before being used.

The propylene carbonate (PC), LiCF_3SO_3 and lithium metal were purchased from Aldrich Chemical Co. The PC was purified by percolation through molecular sieves (5A type zeolite, dried at 400°C for two days under vacuum), followed by destination under vacuum. It was then stored over molecular sieves in an Argon-filled glove box. LiCF_3SO_3 was dried at 160°C for three days in a vacuum before it was mixed with PC.

Electrode Preparation

The solid positive electrode of black carbon-mixed zeolite was prepared in the same way as that of black carbon-mixed clay, that is, we mixed intimately the dried black carbon and zeolite first and then pressed this mixing powder into a pellet of 1.2 cm in diameter. Finally, this pellet was set into a battery cell which is the same as that in reference [6]. The whole preparation process was done in an Argon-filled glove box. We must emphasize that all the results shown in this paper were obtained from the 20 weight % black carbon-mixed zeolite or clay solid electrodes and all the electrochemical tests were done in the Argon-filled glove box.

Measurements

The lithium electrochemical testing was done by using the MacPlie from the BioLogic Co. (France) and this equipment has 16 electrochemical testing channels controlled by the MacPlie software in a Macintosh computer.

RESULTS AND DISCUSSION

Fig. 1 and Fig. 2 are the galvanostatic charge and discharge cycles for 20 weight % black carbon-mixed 13X type zeolite and VSP-200 clay electrodes respectively. To compare these two electrodes with the different weight of active materials and different battery cells, we set the experimental parameters in such a way that: (1) both clay and zeolite have the same molecular weight; (2) with the same energy density allowed for both cathode electrodes even under the different charge and discharge current, this energy density is equal to 100 mAh/g. We can see that under the applied current density of $30 \mu\text{A}/\text{cm}^2$, the black carbon-mixed zeolite electrode has a higher discharge potential and a smaller structural polarization for both anodic and cathodic processes. Especially after several "formatting" cycles, the charge and discharge potentials are stabilized in 1.7 and 1.1 volts respectively even under the charge and discharge applied current density of $100 \mu\text{A}/\text{cm}^2$. Presently we have had about 20 stable cycles as a cyclability. Unlike the clay electrode [6], the reason for the difference between the first several "formatting" cycles and the cycles after that for zeolite electrode is not yet clear.

Fig. 3 shows the voltage vs. time (which is also proportional to composition x in Li_x (zeolite)) diagram for 13X and 4A types of zeolite electrodes that have been

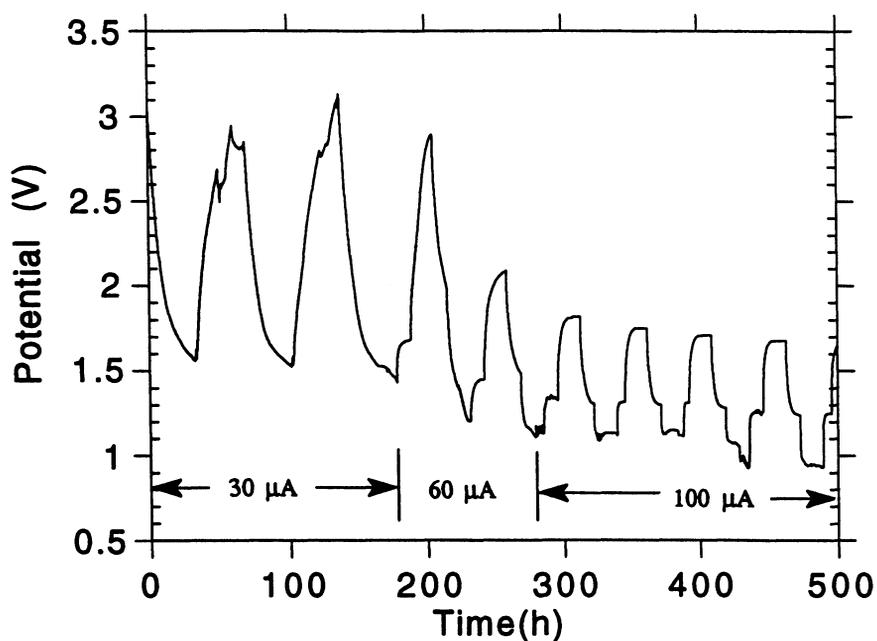


FIGURE 1 The galvanostatic charge and discharge cycles for black carbon mixed 13X type zeolite electrode.

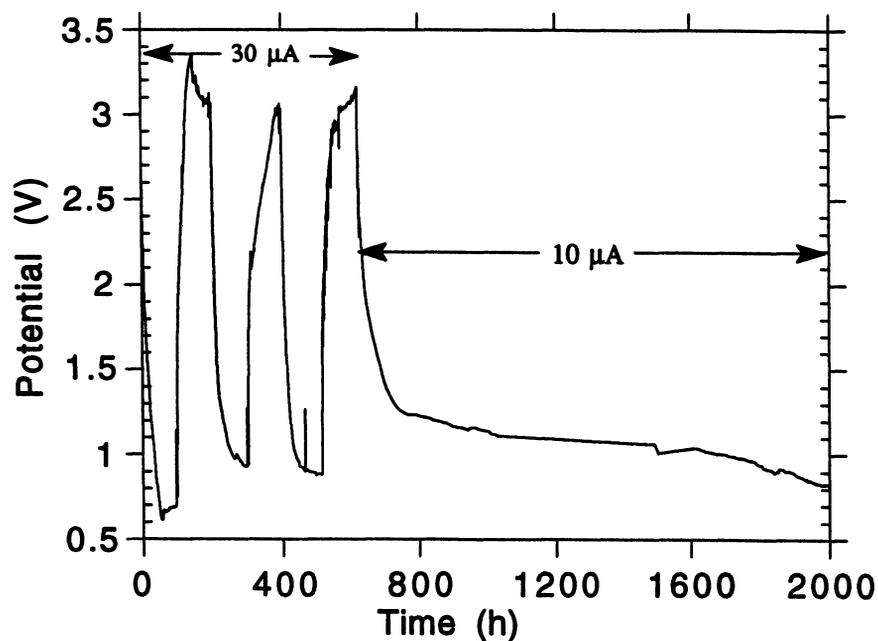


FIGURE 2 The galvanostatic charge and discharge cycle for black carbon mixed VSP-200 type clay electrode.

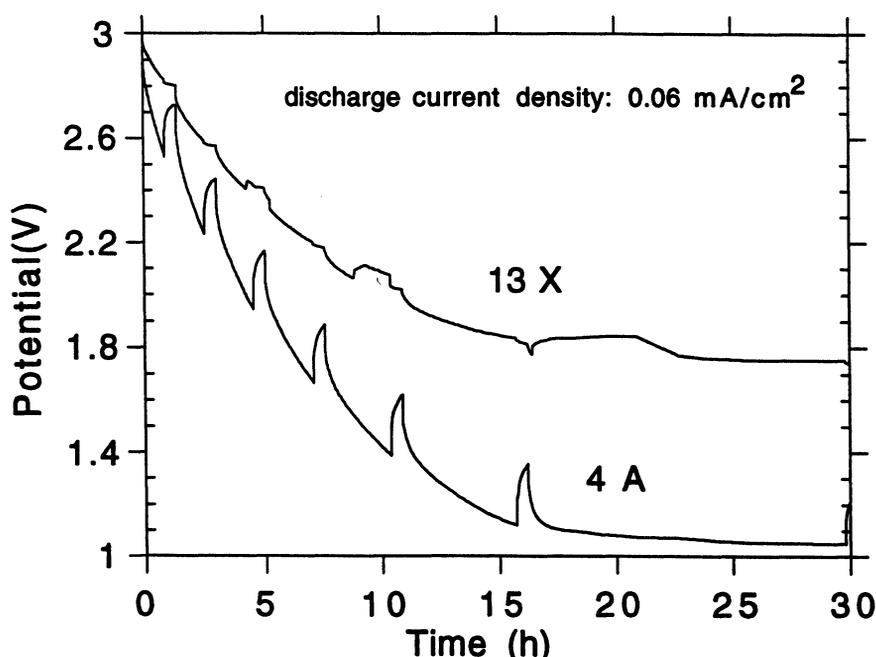


FIGURE 3 The discharge potential vs time with the relaxation process for 4A and 13X types zeolite electrodes.

undertaken with two charge and discharge cycles and then have been discharged under $60 \mu\text{A}/\text{cm}^2$ with relaxation times in order to obtain the thermodynamic curve. The total discharge and relaxation duration is about 30 hours, and with this applied current density, this time corresponds to an energy density of 100 mAh/g). The relaxation is interrupted when the slope of the voltage vs time curve is smaller than 0.1 mV per hour. For the 13X type zeolite, the equilibrium is reached very quickly and corresponds to a relatively small potential drop during the whole discharge process compared to that for the 4A zeolite type. This behavior characterizes a higher kinetics of intercalation, which is mainly due to the large size of tunnels (such as cages, pores and interconnected voids) of 13X type zeolite compared to that of 4A type zeolite's. However, unlike the charge and discharge behaviors under applied current density of $100 \mu\text{A}/\text{cm}^2$, we could not find a very strong variation in voltage under the discharge current density of $60 \mu\text{A}/\text{cm}^2$ (see Fig. 1).

Fig. 4 and Fig. 5 show the comparison of discharge voltage vs composition under different current densities for 13X type zeolite and SuperLig type clay electrodes. Here, to compare these two electrodes easily, we assumed that the molecular masses for clay and zeolite are the same, namely 450. Correlated to the discussion above, the zeolite electrode has a higher discharge voltage output than the clay electrode with the same amount of energy density. For zeolite, the energy density under $60 \mu\text{A}/\text{cm}^2$ discharge current can be an order of 200 mAh/g compared to 150 mAh/g of the clay electrode while the power density reaches 300 mW/g compared to

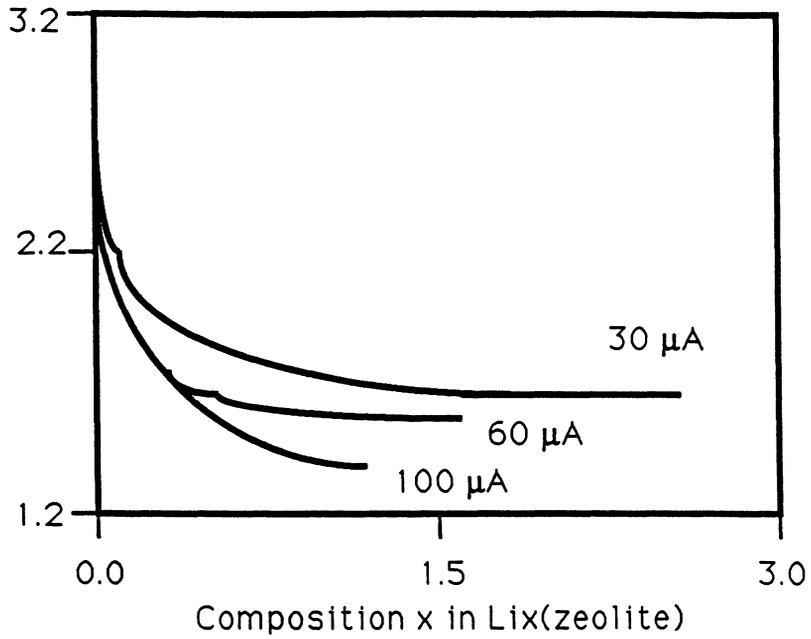


FIGURE 4 The discharge potential vs composition for black carbon mixed 13X type zeolite electrodes under different applied current densities.

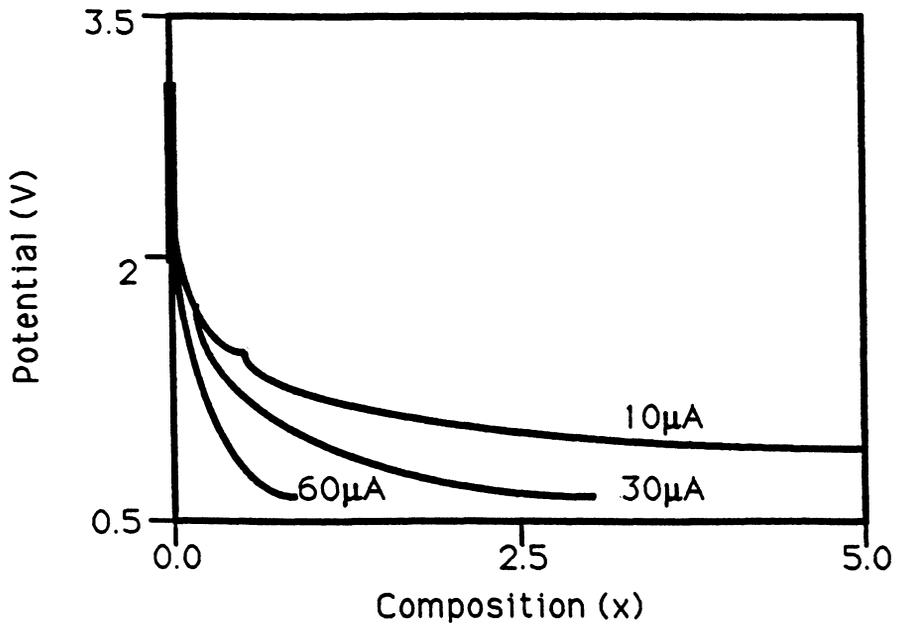
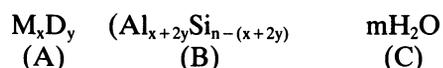


FIGURE 5 The discharge potential vs composition for black carbon mixed SuperLig type clay electrodes under different applied current densities.

100 mW/g of the clay electrode. This calculation is done by considering that zeolite and clay are the only active materials in black carbon-mixed composite electrodes.

What are the explanations corresponding to these experimental results upon the black carbon-mixed zeolite electrode? We know that the structure of zeolite is interesting in many respects. Zeolite can be considered as crystalline aluminosilicate polymers that are obtained by the building of a three dimensional network of AlO_4 and SiO_2 tetrahedra linked by the sharing of oxygen atoms. The geometric arrangement is also such that it excludes Al-O-Al bonds as much as possible [6]. The framework thus obtained contains pores, channels, and cages, or interconnected voids. As trivalent aluminum ions replace, to a given amount (depending on the nature of the zeolite), tetravalent silicium ions at lattice positions, the network bears a net negative charge that must be compensated for by counterions (cation). The latter are mobile and may occupy various exchange sites depending, for example, on their radius, charge, or degree of hydration. They can also be replaced, to various degrees, by exchange with other cations. Because of the need to maintain electrical neutrality, there is, of course, a direct 1:1 relationship between the aluminum content of the framework and the number of positive charges provided by the exchange cations.

Considering again the general formula of zeolite, one can then view their chemical structure as shown in the following:



where, A: exchangeable cations; moving species; located at so-called exchange sites; B: aluminosilicate three-dimensional framework which includes well-defined pores, channels, and cages; C: intracrystalline water which can be removed, sometimes reversibly [7].

In our case, the zeolite used in the composite electrode are 4A and 13X types. The 4A type zeolite has the framework in which the sodalite units are linked together by oxygen bridges between the four-membered rings and has the chemical formula of $(Na_{12}Al_{12}Si_{12}O_{48} \cdot 27H_2O)_8$ with 4 Å large 3D tunnels, while 13X type zeolite has the framework in which the sodalite units are linked together by oxygen bridges between the six-membered rings and has the chemical formula of $[(Na_2, Ca, Mg)_{29}Al_{58}O_{384} \cdot 24OH_2O]$ with the 13 Å large of 3D tunnels. So the ion mobility in the three dimensional cages can be assured. In our experimental condition, we think that the water content in two solid electrodes should be much lower than the amount shown in the chemical formulas due to the pre-drying procedure. So the other alkaline ions such as lithium ions can be intercalated and deintercalated reversibly into/from the zeolite compound. Since 13X type zeolite has larger tunnels (13 Å) than that of 4A type zeolite (4 Å), we have found the structural polarization corresponding to charge and discharge processes is smaller in zeolite than in clay.

As zeolites have large 3D tunnels instead of 2D layers in the case of clay, these open frameworks seem to have more accessible sites. The discharge potential is enhanced considerably for the zeolite electrode compared with that for the clay electrode. This also gives us evidence that the charge and discharge potential can

be modulated by choosing judiciously not only the different electric conducting compounds, but also the different porous compounds and in this way, we can improve the discharge energy capacity of the electrode. The particular structural properties of zeolite, e.g., the presence of pores or windows, channels, and cages, with various arrangements and sizes, can be intimately reflected in their intercalation property as well as in their catalytic, diffusional properties.

Based on all these results upon the black carbon mixed zeolite and clay electrodes, we can put forward a new approach for lithium intercalation material for battery applications. This approach requires only a composite in which one compound can offer reversible, neutral, and large enough sites for intercalation guests such as lithium ions and the other compound is capable of circulating electrons back and forth reversibly (electron delocalization role). The first compound can be any kind of chemical and electrochemical stable porous, layered, or tunnel materials and the second compound can be principally any kind of chemical and electrochemical stable metallic materials. In our particular case, we have chosen clay and zeolite compounds for the first candidate, and black carbon for the second. But our approach can be extended to other kind of combinations with different candidates. Since there is no apparent redox couple in these composite electrodes, this approach does not require a redox reaction, which is considered to balance the electrical neutrality during lithium electrochemical intercalation and deintercalation processes. So, the charge and discharge potential can be controlled and modulated by both compounds in this composite, and most importantly, the electrode should be very electrochemically and chemically stable due to the absence of the redox couple.

It is useful to continue to search for the new composite electrodes with high energy density used in lithium battery cell. This approach can be a guide towards further research for new intercalation material and can have importance in rechargeable battery applications.

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REFERENCES

1. J.B. Goodenough, *Solid State Microbatteries, Series B: Physics Vol. 217*, p.213, NATO ASI Series.
2. J.B. Goodenough, *Solid State Microbatteries, Series B: Physics Vol. 217*, 177, NATO ASI Series.
3. M. Stnaley Whittingham, *Prog. Solid St. Chem. Vol. 12*, pp. 41-99, 1978.
4. D. Guyomard, J.M. Tarascon, *J. Electrochem. Soc.*, Vol. 139, No. 4, April 1992.
5. E.G. Derouane, "Intercalation Chemistry," p. 101, Academic Press, Inc., New York, 1982.
6. S.J. Wen, X.T. Yin, L. Nazar, "The new phenomena of lithium electrochemical (de)intercalation in mineral clay materials and their potential application in rechargeable batteries," *Active & Passive Electronic Components*.
7. D.W. Breck, "Zeolite molecular sieves," Wiley, New York, 1974.



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