

Short communication

# Improved cycling performance of nano-composite $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$ as a lithium battery cathode material

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## Abstract

We have recently reported our success in identifying a family of new polyanion cathode materials, namely  $\text{Li}_2\text{M}'_2(\text{MoO}_4)_3$  [ $\text{M}' = \text{Ni}, \text{Co}$  and  $\text{Mn}$ ] and synthesized these polyanion derivatives using soft-combustion based solution synthesize technique. It is known that the polyanion cathode materials reported hither to suffer invariably from intrinsic lattice electronic conductivities regardless of their structure. The new polyanion materials reported by us also suffer from low lattice electronic conductivity. Considering its lithium rich phase to be useful for battery application, we attempted to improvise the electronic conductivity of  $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$  by adding mesoporous (nano-sized) non-graphitized carbon black (NCB) particles as an additional conductive additive together with acetylene black and compared its electrochemical performance with the conventional composite electrode having acetylene black as a conductive additive. The test electrode fabricated with NCB as conductive additive has profound effect on the discharge properties by enhancing the grain–grain contact much more effectively and establishing much better intimacy between the electrode-active grains and thus improving the overall electronic conductivity of the composite electrode. As a result, we found that the conventional composite positive electrode yielded a first discharge capacity of  $26 \text{ mAh g}^{-1}$  between 4.9 and 2.0 V, whereas the nano-composite electrode yielded a discharge capacity of  $86 \text{ mAh g}^{-1}$  which is approximately a four-fold increase. It was also observed that NCB addition facilitated the extended cycling performance in terms of lithium insertion and structural stability retention of the host cathode material.

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**Keywords:** Polyanions; Cathode materials; Lithium nickel molybdate; Mesoporous conductive additive

## 1. Introduction

Rechargeable lithium batteries have become inseparable commodity in a vast array of mobile applications, from micro medical devices to high power automotive. Recent innovations in Li-ion batteries have propelled the technology into a position in the marketplace to fulfill the portable power requirements in the first place. It is well known that such batteries gain pride as the advanced power source technology and are classified under smart power source of the future. However, the present day positive electrode material, lithium cobalt oxide, is expensive and only 50% of its theoretical capacity could be utilized in practical cells, due to chemical and structural instabilities, and safety concerns at deep charge. These difficulties have generated immense interest in the development of alternative cathode materials. Var-

ied research activities are being carried out with a goal to replace the highly toxic  $\text{LiCoO}_2$  in commercial lithium-ion cells.

Currently, high energy density lithium storage systems are the focus of intense interest and expectation. In this perspective, polyanion materials sound very exciting due to their high cell voltage, structural and electrochemical stability, low cost and non-toxicity. Polyanions cover both the NASICON [1–3] and Olivine [4–6] structured compounds that are expected to play a vital role as electrode-active materials in the next generation lithium-ion batteries. The performance and safety of the new cathode materials are the kind of things needed to make a good, low-cost battery. In 1997, researchers at the University of Texas [4] proposed a new cathode material,  $\text{LiFePO}_4$  (theoretical specific capacity =  $170 \text{ mAh g}^{-1}$ ) with an ordered Olivine structure, which is cheaper and safer than  $\text{LiCoO}_2$ . Although  $\text{LiFePO}_4$  fulfills all the required criteria to be a candidate cathode material for Li-ion batteries, it has one big problem being its too low electronic conductivity [7,8].

Although all the polyanion materials investigated so far exhibit reversible electrochemical lithium extraction/insertion

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over a considerable number of cycles, they have the low electronic conductivity ordeal, which stems from their insulating nature [2,9]. Of late, several techniques have been adopted to alleviate this setback, which include the addition of an electronically conducting substance such as carbon or dispersed metal powders during the synthesis itself. These attempts were found to be lucrative if the electronic conductivity of the polyanion materials is at a premium.

Chiang and coworkers [10] at the Massachusetts Institute of Technology had spiced lithium iron phosphate with small amounts of metal ions, such as aluminum, niobium, and zirconium in doping which enhanced the electronic conductivity 10 million times that of pure  $\text{LiFePO}_4$ . Nevertheless, there are some ambiguities due to the nature of starting materials like metal alkoxides, etc.

Huang et al. [11] and Prosini et al. [12] obtained noteworthy improvements by using nano-composites of  $\text{LiFePO}_4$  by a combination of intimate mixing with a graphite precursor containing carbon. Specifically, at 5C rate, the capacity increases on initial cycling to reach a maximum at  $\sim 120 \text{ mAh g}^{-1}$ , with  $\sim 8\%$  loss over 800 cycles. This good rate capability and excellent reversibility was achieved by controlling the particle size to nanometer dimensions [11]. Hydrothermal/mechanical activation process was employed to synthesize  $\text{LiFePO}_4$ , by adding carbon (5 wt%) during synthesis, an initial capacity of  $160 \text{ mAh g}^{-1}$  at room temperature was obtained with a capacity fading of less than 1% on 20th cycle [13]. Quite recently, introduction of carbon as a conductive additive was found to be beneficial in terms of active material utilization and the electrical conductivity of the electrode [14].

Carbon gel was used during hydrothermal synthesis at elevated temperature and the material retained 80% of the theoretical capacity on cycling at room temperature [15]. Doeff et al. [16] were able to enhance the electrochemical performance of  $\text{LiFePO}_4$  by incorporating small amounts of a polyaromatic additive during sol–gel synthesis to produce a carbon coating.

This work was intended to enhance the electrode conductivity of recently identified NASICON type polyanion material  $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$  [2] by adding nano-sized (mesoporous), high surface area activated carbon as conductive additive with a view to improve the composite electrode conductivity and studied the cycling performance and compared it with earlier report. The present study proved that nano carbon (mesoporous) addition indeed effectively improved the overall cycling behaviour of this new polyanion cathode material.

## 2. Experimental

Fine powders of lithiated nickel molybdate,  $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$  were obtained through a simple soft-combustion synthesis route at temperatures as low as  $250^\circ\text{C}$  as described in our previous work [2].

All techniques pertaining to the physical characterization of the material were already mentioned and explained explicitly [17]. Investigation on the electrochemical lithium extraction/insertion properties of  $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$  were made using Arbin Instruments BT 2000 series battery-testing system. Test

cells were composed of a composite cathode (working electrode) and a thin lithium foil as both reference and counter electrode.

In order to improve the conductivity of  $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$ , highly conducting nano-sized carbon black (NCB) [Monarch 1400, Cabot Inc., USA, BET surface area:  $469 \text{ m}^2 \text{ g}^{-1}$ ; grain size: 13 nm;  $\sigma_e$ :  $19.7 \text{ S cm}^{-1}$ ] was used as conductive additive in addition to the conventional acetylene black (AB), [BET surface area:  $120 \text{ m}^2 \text{ g}^{-1}$ ; grain size: 0.1–10  $\mu\text{m}$ ;  $\sigma_e$ :  $10.2 \text{ S cm}^{-1}$ ]. Nano-composite positive electrode (cathode) consisted of 65% active material, 5% binder (PTFE) and 30% conducting carbon mixture. The conducting carbon mixture comprised of an equal proportion of AB and NCB (nano-sized particles exhibiting mesoporosity of 3–10 nm). The contents were thoroughly hand mixed with mortar and pestle. Nano-composite positive electrodes were fabricated following the procedure given earlier [2,17]. The fabricated cells were allowed to equilibrate for 24 h inside argon filled insert box.

## 3. Results and discussion

The results concerning the phase formation temperature, phase purity and structure of the synthesized powders, calculation of unit cell parameters, electronic state of different elements present and metal content of the synthesized product were already reported [17]. The redox properties of  $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$  were demonstrated by means of electrochemical techniques such as slow scan cyclic voltammetry (SSCV) and constant current galvanostatic charge/discharge test. The results of the first 10 charge/discharge cycles were presented along with an appropriate explanation for different redox couples operating on the oxidation and reduction processes during charge and discharge of the cell. The first two galvanostatic charge/discharge cycles and the quantitative amount of lithium involved in the reversible process were also reported previously [2,17]. Also, we confirmed the facile reversible electrochemical characteristics of  $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$ .

To investigate the effect of nano-sized carbon black on the electrochemical behaviour of  $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$ ,  $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$ [nano-composite cathode]/Li half-cells were tested under galvanostatic conditions between 4.9 and 2.0 V at low current densities:  $2.5 \text{ mA g}^{-1}$  (charge) and  $1.25 \text{ mA g}^{-1}$  (discharge). Our previous result on the conventional electrode is also taken for comparison.

The first charge/discharge curves obtained using the nano-composite positive electrode (with NCB) are compared to the first charge/discharge curves of the conventional electrode (without NCB) as shown in Fig. 1. Fig. 1 shows the clear evidence for the difference between the two cases in terms of IR drop, the amount of lithium inserted and shape of the discharge profiles. The diminished IR (ohmic) drop (4.9–4.73 V) at the beginning of the discharge process after charge in the case of the nano-composite electrode is well seen in Fig. 1 (inset). But, in the conventional case, a large IR (ohmic) drop was observed (4.9–4.5 V). No obvious changes were observed in terms of  $\text{Li}^+$  extraction (charge) between the nano-composite electrode and conventional composite electrode. In both cases,  $\sim 1 \text{ Li}^+$  per formula unit was extracted up to a potential of 4.9 V (charge

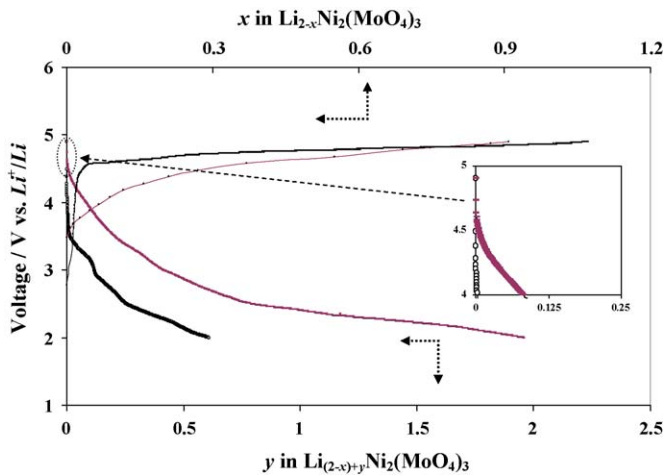


Fig. 1. Comparison of first charge/discharge of nano-composite  $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$  and conventional  $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$  against lithium between 4.9 and 2.0 V. Inset: discharge curves showing the difference in the IR (ohmic) drop between the two electrodes. Charge current density:  $2.5 \text{ mA g}^{-1}$ ; discharge current density:  $1.25 \text{ mA g}^{-1}$ ; weight of the active material: 0.065 g; electrolyte: 1 M  $\text{LiPF}_6$  (EC/DMC).

cut off) versus  $\text{Li}^+/\text{Li}$  during the first charge. As for the discharge (lithium insertion reaction), the former electrode shows a considerable improvement in the first discharge process, during which  $\sim 2 \text{ Li}^+$  was inserted down to 2.0 V (discharge cut off) corresponding to a discharge capacity of  $86 \text{ mAh g}^{-1}$  which is approximately a four-fold excess compared to our earlier studies wherein we obtained only  $26 \text{ mAh g}^{-1}$  ( $0.6 \text{ Li}^+$  down to 2.0 V).

Apart from the above changes observed, a smooth discharge profile of the nano-composite electrode right from the beginning down to 2.0 V is note worthy; whereas the conventional electrode seems to exhibit two-slope feature during the first discharge that appears distinctly on the discharge plateau. These significant changes observed in the discharge profile clearly demonstrate the role of addition of non-graphitized carbon black (nano-sized) on the electrochemical properties of the host cathode.

Fig. 2 presents the multiple charge/discharge curves (first 20 cycles) of  $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$  [conventional cathode]/Li cell cycled

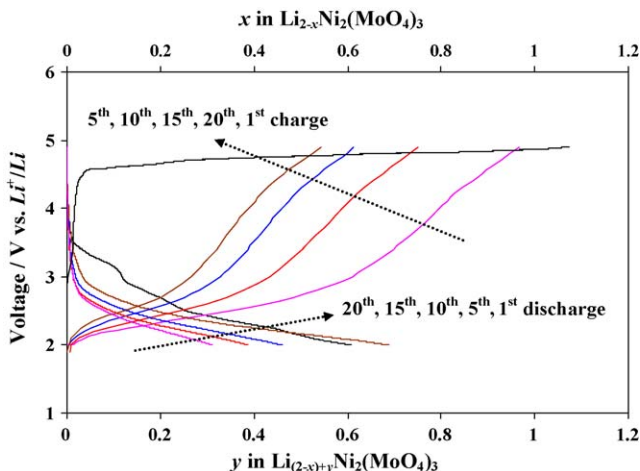


Fig. 2. Galvanostatic multiple charge/discharge of conventional  $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3/\text{Li}$  cell. Experimental conditions: same as in Fig. 1.

Table 1

Enhanced electrochemical properties of nano-composite  $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$  compared to conventional  $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$

Cycle number	Electrochemical properties of $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$ positive electrode			
	Conventional composite cathode <sup>a</sup>		Nano-composite cathode <sup>b</sup>	
	Amount of $\text{Li}^+$ inserted down to 2.0 V	Discharge capacity ( $\text{mAh g}^{-1}$ )	Amount of $\text{Li}^+$ inserted down to 2.0 V	Discharge capacity ( $\text{mAh g}^{-1}$ )
1	0.6	26	2	86
5	0.7	30	0.8	36
10	0.5	20	0.78	35
15	0.4	17	0.72	32
20	0.3	14	0.7	29

<sup>a</sup> AB added  $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$ .

<sup>b</sup> AB and NCB added  $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$ .

under the same experimental conditions. It is seen that after the first cycle, there was a change in the shape of the charge and discharge profiles. The distinct potential profile appeared in the first cycle disappeared for the rest of the cycles studied. It is likely that the material had undergone a structural phase transition after the first cycle. In addition, as for the quantity of  $\text{Li}^+$  insertion, we observed a sharp decreasing trend as the cycle number increases as summarized in Table 1.

Fig. 3 shows the multiple charge/discharge curves (first 20 cycles) corresponding to the nano-composite cathode material. There was no difference found in the shape of the discharge curves between the first cycle and the rest of the cycles studied unlike the conventional one (Fig. 2) where the distinct shape of the curves was evident. The amount of  $\text{Li}^+$  inserted in the nano-composite cathode during the 5th, 10th, 15th and 20th discharge was larger than the corresponding values in the conventional one as indicated in Fig. 3. For instance, at the end of 20th cycle, the quantitative amount of  $\text{Li}^+$  insertion was found to be only 0.3 in the conventional composite cathode, whereas, the NCB added cathode was able to accommodate 0.7  $\text{Li}^+$  at the end of 20th cycle. All such improvements in the electrode activity are attributable to the presence of nano-sized carbon black as conductive additive. Nano-sized carbon black plays an active role

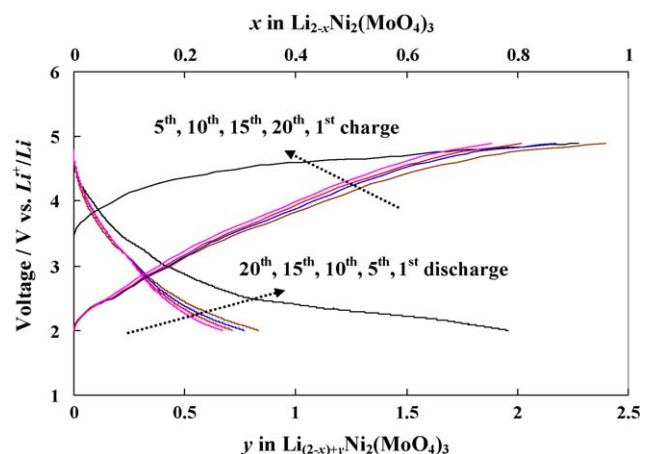


Fig. 3. Galvanostatic multiple charge/discharge of nano-composite  $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3/\text{Li}$  cell. Experimental conditions: same as in Fig. 1.

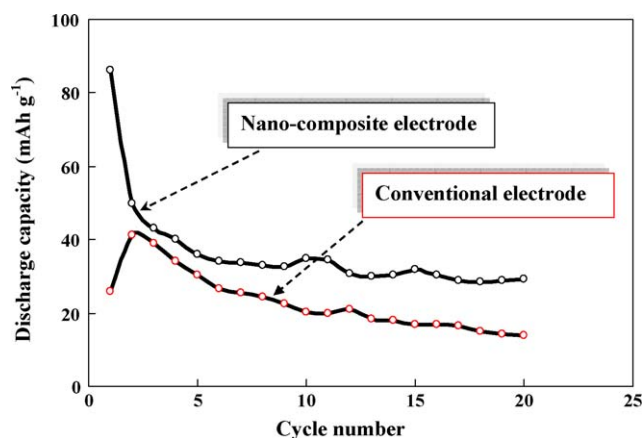


Fig. 4. Plot of discharge capacity of nano-composite  $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$  and conventional composite  $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$  as a function of cycle number.

in enhancing the particle–particle contact of the electrode-active material thus resulting in increased bulk conductivity of the cathode material.

The variation of discharge capacity with cycle number for both types of electrode is shown in Fig. 4 for the first 20 cycles. The discharge capacity delivered by the conventional composite cathode declines tangentially down to  $14 \text{ mAh g}^{-1}$  at the end of 20th cycle. On the other hand, for the NCB added cathode, although the discharge capacity falls from  $86 \text{ mAh g}^{-1}$  (first discharge) to  $50 \text{ mAh g}^{-1}$  (second discharge) due to irreversible capacity, there is no abrupt decrease in capacity as the cycle number increases. Table 1 provides the electrochemical properties to summarize the improvements made on the NCB added cathode over the conventional one. It is seen that NCB addition could improve the cycling behaviour of  $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$ . It appears that the nano-sized grains accompanied by the presence of mesoporosity (see Fig. 5) in the NCB facilitated the

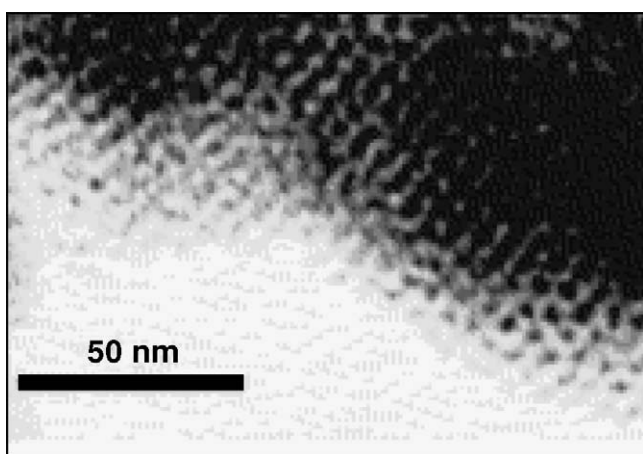


Fig. 5. TEM picture exhibiting mesoporosity of nano carbon black (NCB), Monrach 1400 obtained from Cabot, USA.

enhanced grain–grain contact between the electrode-active particles and provided the enhanced intactness between electrode-active grains and the conductive additive carbons established via PTFE upon repeated charge/discharge cycles. Obviously such intimacy is expected to enhance the electronic conductivity of the overall composite matrix. This may also be the effect of structural stability of the cathode materials upon repeated cycling.

#### 4. Conclusion

We have demonstrated the effect of adding the mesoporous (nano-sized) non-graphiticized carbon black as a conductive additive in  $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$  and compared the cycling performance with a composite electrode prepared without such an additive carbon. The electrochemical properties of both the conventional composite cathode and nano-composite cathode were studied to determine the role of mesoporous carbon as conductive additive. The test electrode fabricated with NCB as conductive additive has profound effect on the discharge properties by enhancing the grain–grain contact much more effectively and establishing much better intimacy between the electrode-active grains and thus improving the overall electronic conductivity of the composite electrode. As a result, a four-fold increase in discharge capacity was confirmed due to NCB addition.

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