

# Novel Manganese Adipate Nanoparticles as Stable Anode Materials for Lithium-ion Batteries

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It is important to seek inexpensive and environmentally friendly electrode materials for energy storage and conversion. Manganese adipate coordination polymer nanoparticles are first found to be an anode material for lithium-ion batteries. The second discharge capacity of the anode is as high as 439 mAh g<sup>-1</sup> at a current density of 200 mA g<sup>-1</sup>. A reversible capacity of 454.8 mAh g<sup>-1</sup> remained after 100 cycles. In addition, a reversible reaction mechanism was proposed.

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**Keywords:** Coordination polymer; Lithium-ion battery; Dicarboxylic acid

## 1. INTRODUCTION

Currently, development of a secondary battery for hybrid electric vehicles is important to reduce environmental pollution[1, 2]. Lithium-ion batteries are promising candidates due to their high energy density and long cycling life[3]. However, commercially available material-graphite intercalation anode has a low discharge capacity of 372 mAh g<sup>-1</sup>, which has limited the large-scale application of lithium-ion batteries. Great interest has been drawn to seek new anode and cathode materials with high energy density, easy synthesis, low cost and long cycling stability.

Recently, coordination polymers and metal organic framework have been widely investigated in energy storage for various compositions and crystalline structures, for example, lithium-ion batteries [4-7], sodium-ion batteries[8-13], potassium-ion batteries [14-16] and Li-S batteries[17]. Current research has determined that manganese, zinc and cobalt dicarboxylates can be stable anode materials for lithium- [8] and sodium-ion batteries [9]. However, the involved dicarboxylic acids are 2,5-furandicarboxylic acid, pyridine dicarboxylic acid, 2,5-thiophenedicarboxylic acid,

naphthalenedicarboxylic acid and 4,5-imidazoledicarboxylic acid. Most of these acids are very expensive, thus limiting the promising application of transition metal dicarboxylates. Adipic acid can be prepared from a bio-based platform chemical of lignin, which is an alkyl-aromatic polymer present in plant cell walls for defence, structure, and water transport [18]. A recent report has shown that one can employ metabolic engineering, separation, and catalysis to convert lignin-derived species into *cis*, *cis*-muconic acid, for subsequent hydrogenation to adipic acid [18]. However, the application of metal adipates has been few and far between with the exception its magnetic properties [19].

Herein, we prepare new Mn adipate coordination polymer nanoparticles via a facile solvothermal method. When tested as an anode material for lithium-ion batteries, the Mn adipate coordination polymer showed a high discharge capacity and good cycling stability. X-ray diffraction (XRD) and FT-IR were further performed to identify the crystalline structure of the charge-discharge products, and we determine the possible electrochemical reaction mechanism of Mn adipate coordination polymer.

## 2. EXPERIMENTAL

All reagents were used as received. Synthesis was performed via a solvo-hydrothermal method in an absolute alcohol-water mixed solvent. The reaction of equal mmol adipic acid and manganese (II) acetate tetrahydrate was performed in the absolute alcohol-water mixed solution and stirred for 2 h. After that, the white solution was transferred to a autoclave, sealed, held at 200 °C for 24 h, cooled, washed and dried at 80 ° C for one night.

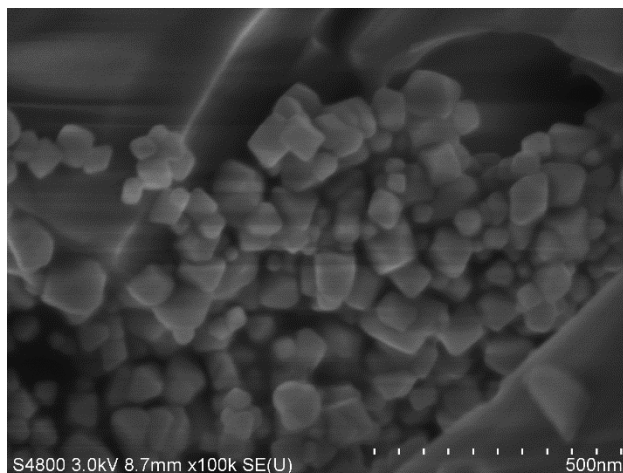
SEM was observed with a Hitachi S-4800 field emission scanning electron microscope. X-ray diffraction (XRD) was performed with PANalytical and X'Pert diffractometers. FT-IR spectra were obtained with an America Thermo-Fisher Scientific Nicolet 6700 spectrometer. The cycling performance of the batteries was tested with a Land CT2001A battery tester. The content of H, C, N was obtained with a German Varo EL elemental analyser. Cyclic voltammetry (CV) was tested with a Chi660c electrochemical workstation.

Manganese adipate nanoparticles were found to work as an anode material for lithium-ion batteries. We pasted the active material, a conductive material (super-pure carbon) and binder polyvinylidene difluoride (PVDF) to a Cu foil in a weight ratio of 6/3/1 for use as a negative electrode. Li foil was the counter electrode.

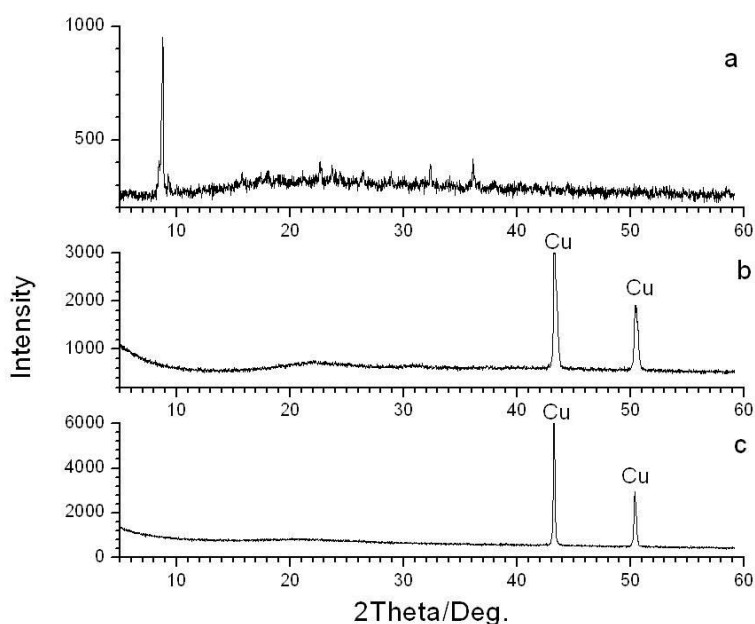
## 3. RESULTS AND DISCUSSION

The SEM image shows that the as-synthesized sample has a morphology of irregular particles with a diameter of ca. 125 nm in Fig. 1. X-ray diffraction displays that these nanoparticles are crystalline not amorphous with a strong peak at 8.854° in Fig. 2a, which is characteristic of coordination polymers and is consistent with  $\text{Mn}_2(\text{H}_2\text{O})[\text{O}_2\text{C}(\text{CH}_2)_4\text{CO}_2]_2$ ; no other peaks are shown [20]. Mn oxide peaks are absent, implying that phase-pure manganese adipate coordination polymer has been prepared. Fig. 3a is the FT-IR spectrum of the coordination polymers. The low-frequency

shift of  $\nu_{\text{asym}}(\text{OCO})$  peak in  $1571\text{ cm}^{-1}$  reveals the absence of free adipic acid and confirms complete coordination with the manganese ion [20].



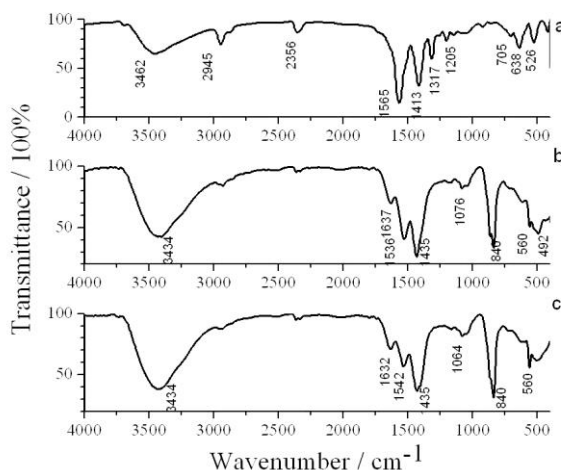
**Figure 1.** SEM image of the as-synthesized coordination polymer



**Figure 2.** Wide-angle XRD pattern of a) the as-synthesized dicarboxylate, b) the 1<sup>st</sup> discharge product and c) the 1<sup>st</sup> charge product.

The infrared spectrum of manganese adipate exhibits two bands at  $1565$  and  $1413\text{ cm}^{-1}$ , which are characteristic regions for the  $\nu_{\text{a}}(\text{OCO})$  and  $\nu_{\text{s}}(\text{OCO})$  bands [21]. The bands in the region ca.  $638$ – $1317\text{ cm}^{-1}$  are attributed to  $-\text{CH}-$  in-plane or out-of-plane bending [22]. The band of  $2945\text{ cm}^{-1}$  is characteristic of  $\nu_{\text{C-H}}$  vibration modes of the  $-\text{CH}_2-$  groups within the carbon chain of adipic acid [22]. The broad band ca.  $3325\text{ cm}^{-1}$  of the vibrations of the coordination water does not appear. The broad band at approximately  $3462\text{ cm}^{-1}$  is ascribed to the absorbing OH stretching vibration [23]. EA was performed to detect the molar ratio of C to H with a value of 0.68, which is very close to the value of

0.75 when adipic acid loses two H atoms and one O atom. Therefore, the formula of manganese adipate was estimated to be  $\text{MnC}_6\text{H}_8\text{O}_3$ .

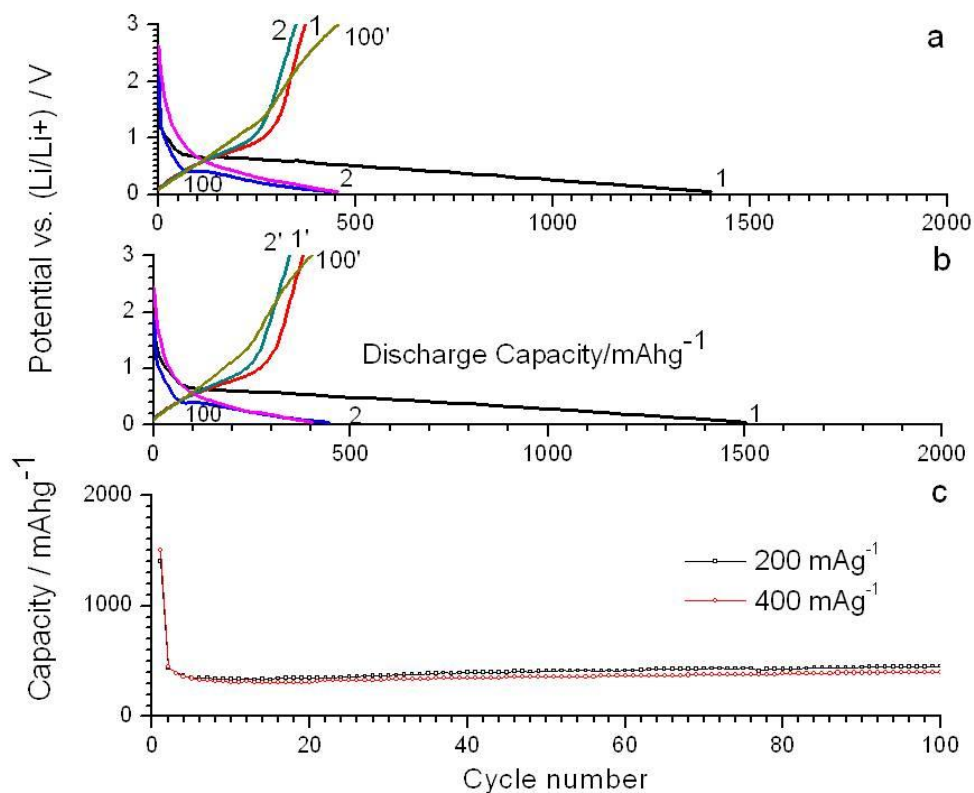


**Figure 3.** FT-IR spectra of a) the dicarboxylate, b) the 1<sup>st</sup> discharge product and c) the 1<sup>st</sup> charge product.

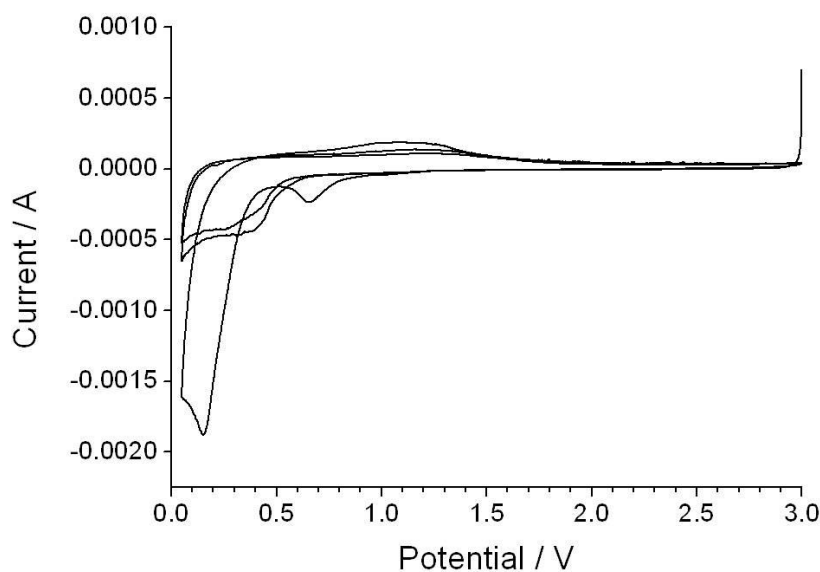
The electrochemical performance of manganese adipate nanoparticles was evaluated in lithium-ion batteries. Fig. 4a show the 1<sup>st</sup>, 2<sup>nd</sup>, and 100<sup>th</sup> charge-discharge curves at 200 mA g<sup>-1</sup>. The 1<sup>st</sup>, 2<sup>nd</sup>, and 100<sup>th</sup> discharge capacities are 1401.9, 439, and 453.2 mAh g<sup>-1</sup>, respectively. Fig. 4b shows the 1<sup>st</sup>, 2<sup>nd</sup>, and 100<sup>th</sup> charge-discharge profiles at a current density of 400 mA g<sup>-1</sup>. The 1<sup>st</sup>, 2<sup>nd</sup>, and 100<sup>th</sup> discharge capacities are 1501.8, 445.5, and 401.4 mAh g<sup>-1</sup>. It can be seen that both have similar discharge curves with an inflexion, implying that a reversible electrochemical reaction occurred at different current densities. The discharge capacity is higher than that of commercially available graphite electrode materials. Fig. 4c shows the manganese adipate electrode materials have a stable capacity at current densities of 200 and 400 mA g<sup>-1</sup>. For comparison, we list the reported anode materials based on carboxylates in Table 1. The summary shows that carboxylate-based anode materials often have good cycling stability, while transition metal (Zn, Mn, Co and Ni) dicarboxylates have a higher discharge capacity than those of their Li and Ca counterparts. Manganese adipate nanoparticles in this work have a comparable capacity comparable to that of Zn and Mn dicarboxylate coordination polymers.

XRD was used to investigate the 1<sup>st</sup> and 2<sup>nd</sup> discharge products in Fig. 1b,c, which were found to be amorphous. Fig. 2b and c are the FT-IR spectra of the 1<sup>st</sup> and 2<sup>nd</sup> discharge samples in Fig. 2b and c. Both the 1<sup>st</sup> and 2<sup>nd</sup> discharge products have the same IR spectra, but they differ from manganese adipate before charging and discharging. The results show that manganese adipate was converted to a new manganese adipate after the first discharge. The new manganese adipate can be reversible intercalation and deintercalation after the following cycles. The lithium intercalation for manganese adipate was also studied by cyclic voltammetry (CV). The 1<sup>st</sup> CV curve shows two cathodic peaks at 0.15 and 0.65 V in Fig. 5, which are ascribed to the intercalation of a conductive material (super-pure carbon) and the formation of new manganese adipate coordination polymer. In

the following cycles, one cathodic peak appears at approximately 0.4 V for the second and third cycles, and the peak can be ascribed to the intercalation of newly formed manganese adipate.



**Figure 4.** The charge–discharge curves of manganese adipate nanoparticles at current densities of (a) 200 mA g<sup>-1</sup> and b) 400 mA g<sup>-1</sup>, and c) the corresponding cycling performance.



**Figure 5.** Cyclic voltammograms of manganese adipate nanoparticles.

**Table 1.** The reported coordination polymer anode materials for LIBs.

Ref.	Materials	Acid	Current density (mA g <sup>-1</sup> )	Capacity (mAh g <sup>-1</sup> )	Cycle number
[24]	Li <sub>5</sub> Zn <sub>6</sub> C <sub>25</sub> H <sub>11</sub> N <sub>10</sub> O <sub>24</sub>	4,5-imidazole dicarboxylic	50	75	100
[25]	Manganese dicarboxylate	2,5-thiophene dicarboxylic	400	645.7	250
[26]	[Mn <sub>2</sub> (pdc) <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ] <sub>n</sub> ·2nH <sub>2</sub> O	Pyridine-2,3-dicarboxylic	500	457.2	100
[27]	Zn 2,6-pyridinedicarboxylate	2,6-pyridinedicarboxylate	750	569.7	200
[9]	Zinc naphthalenedicarboxylate	1,4-naphthalenedicarboxylic	100	468.9	100
[28]	[Co <sub>1.5</sub> L(H <sub>2</sub> O) <sub>4</sub> ] <sub>n</sub>	4-hydroxypyridine-2,6-dicarboxylic	50	431	431
[29]	Ni-BHC	1,2,3,4,5,6-benzenehexacarboxylic	200	1437.2	1437.2
[30]	dilithium thiophene-2,5-dicarboxylate	2,5-thiophene dicarboxylic	549	30	50
[31]	[Mn(3,5-PDC)centre dot 2H(2O)]	3,5-pyridinedic	100	554	240

			arboxylic			
	Mn 2,5-furandicarboxylate	2,5-		100	436.6	206
			furandicarb			
			oxylic			
[32]	cobalt	2,3,5,6-	2,3,5,6-	100	1074.6	50
	tetrafluoroterephthalic		tetrafluoroterephthalic			
[33]	CoCOP nanowires			200	760	100
[34]	Mn <sub>2</sub> (NDC) <sub>2</sub> (DMF) <sub>2</sub>	1,4-naphthalene		765.4	200	300
			dicarboxylate			
			te			
[35]	Calcium terephthalate	terephthalic acid		50	161	26
[36]	([Zn(4,4'-bpy)(tfbdc)(H <sub>2</sub> O) <sub>2</sub> ])	tetrafluoroterephthalic		50	623	100
[37]	Cobalt-terephthalonitrile	terephthalonitrile		100	1132	100
[38]	Zn-ODCP	3-methyl-1H-pyrazole-4-carboxylic acid		50	300	50
		2,3,5,6-tetrafluoroterephthalic acid				
[39]	Co-Zn-MOF	terephthalic acid		2000	622	500

#### 4. CONCLUSIONS

In summary, an inexpensive bio-based chemical adipic acid platform was used for the preparation of coordination polymer manganese adipate nanoparticles. Manganese adipate was a promising anode material for lithium-ion batteries. In addition, this work shows the potential applications of other linear dicarboxylic acid-based materials for energy storage. Further work should be concentrated on applying non-conjugated dicarboxylate to secondary batteries.

#### ACKNOWLEDGEMENTS

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