



Short communication

Nanocomposite of manganese ferrocyanide and graphene: A promising cathode material for rechargeable lithium ion batteries



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ABSTRACT

A nanocomposite of potassium manganese ferrocyanide and graphene (12% C, 88% $K_{1.8}Mn_{1.1}Fe(CN)_6 \cdot 0.27H_2O$) was prepared by ball milling of graphene oxide powder and nanoparticles of manganese–iron Prussian Blue. It exhibits enhanced electrochemical performance compared to pure Prussian Blue with a specific capacity of 150 mAhg^{-1} at average 3.8 V vs. Li^+/Li and a good cyclability. The nanocomposite can be considered as competitive to standard cathode materials of present rechargeable lithium ion batteries like cobalt oxide, iron phosphate or NMC.

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1. Introduction

Currently, state-of-the-art cathodes of rechargeable lithium ion batteries are transition metal oxides [1,2], $LiFePO_4$ has become the phase of choice with 170 mAhg^{-1} at an average potential of 3.5 V [3,4]. Typically oxides are being explored as cathode materials where the oxide anion forms a weak ligand. Strong ligands induce larger ligand field splittings and thus can enhance the electrochemical potentials due to lowering the HOMO states at the metal as in Prussian Blue Analogues (PBA) [5].

The feasibility and lithium intercalation behaviors of several PBA compounds have been investigated in 1990s [6–8]. Until 2004, Eftekhari proposed a potassium secondary cell based on a PBA cathode, showing 75 mAhg^{-1} specific capacities at 3.8 V average potential vs. K^+/K [9]. PBA electrodes are still attracting attention for long-life grid-scale energy storage [10,11]. $K_{0.14}Mn_{1.43}[Fe(CN)_6] \cdot 6H_2O$ and $Rb_{0.7}Mn_{1.15}[Fe(CN)_6] \cdot 2.5H_2O$ show 3.5 V average potential and quite good cyclability with 60 mAhg^{-1} [12,13]. A thin film electrode of $Na_{1.32}Mn[Fe(CN)_6]_{0.83} \cdot 3.5H_2O$ exhibits an interesting two plateau potential of 3.4 V and of 3.9 V vs. Li^+/Li , with 128 mAhg^{-1} in the first cycle and good cyclability [14]. A nanocomposite of graphene and PBA was already synthesized photo-chemically [15,16].

We have chosen manganese ferrocyanide as cathode candidate here. Consequently, nanoparticles of potassium Mn(II) ferrocyanide were synthesized by simple precipitation from aqueous solution and were then combined with graphene nanosheets by mechanical ball-milling

[17–19]. In contrast to other related experiments, potassium ions were extracted electrochemically, and thereafter both redox couples Mn^{3+}/Mn^{2+} and Fe^{3+}/Fe^{2+} were utilized.

2. Experimental

Potassium manganese ferrocyanide (MPB) was synthesized by adding an Mn^{2+} (0.1 M, 100 ml) to a $K_4Fe(CN)_6$ solution (0.05 M, 200 ml) with immediate white colloidal precipitation which was centrifuged and washed with deionized water for a couple of times, thereafter with ethanol, and dried at 60 °C under vacuum overnight.

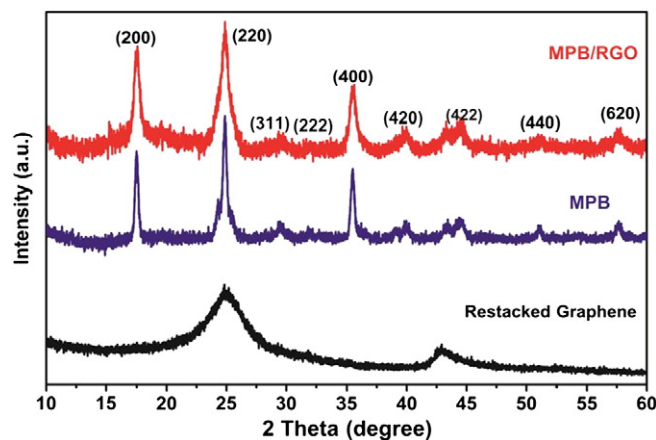


Fig. 1. Powder XRD patterns of MPB, MPB/RGO and restacked graphene.

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Table 1

Experimental and theoretical compositions and maximum specific capacities of composites MPB and MPB/RGO.

		Elemental analysis (wt. %)						Max. specific capacity (mAhg ⁻¹)
		K	Mn	Fe	C	N	H	
MPB: K _{1.8} Mn _{1.1} Fe(CN) ₆ · 0.5H ₂ O	exp.	19.19	16.76	15.57	20.22	23.94	0.28	51
	cal.	20.01	17.18	15.88	20.49	23.89	0.29	137
MPB/RGO: 12% C & 88%K _{1.8} Mn _{1.1} Fe(CN) ₆ · 0.27H ₂ O	exp.	16.67	14.26	13.59	29.35	20.34	0.13	150*
	cal.	17.81	15.30	14.14	30.25	21.27	0.14	140*

*The maximum specific capacities refer to the masses of active materials excluding additives and RGO.

The product was mixed with yellowish graphite oxide powder, which was synthesized as described elsewhere [20]. Then the mixture was ball-milled at 400 rpm for 2 h. The weight ratio of MPB and graphite oxide was chosen to be 4:1, yielding around 10% carbon in the final product. After ball milling, the color of the sample changed from brownish to black indicating to the reduction process to reduced graphene oxide (RGO). The composite of MPB and RGO (MPB/RGO) was then heated under vacuum at 200 °C for 4 h.

Powder X-ray diffraction was performed on a Stoe STADI P powder diffractometer (DectrisMythen Detector, Cu-Kalpha radiation, Gemonochromator). Carbon, nitrogen, hydrogen contents were determined by Micro-elemental-analyses and the metals contents by ICP-OES (Spectro Arcos, SPECTRO Analytical Instruments GmbH, Germany). Scanning Electron Microscopy (SEM) was performed using a Zeiss Gemini 1530 operated at 1 kV. For Transmission Electron Microscopy (TEM), samples were deposited onto a holey carbon foil supported on a copper grid and analyzed on a CM30ST microscope (FEI; LaB₆ cathode) or on a Tecnai F30 microscope (both operated at 300 kV, point resolution 2 Å).

Lithium metal (ribbon 0.5 mm thick, Aldrich) was employed as reference electrode and Merck LP30 as electrolyte consisting of 1 M solution of LiPF₆ in mixture of ethylene carbonate and dimethyl carbonate 1:1 (w/w). Active material, Super P carbon black, and PVDF (80:10:10 wt. %) was ground and ultrasonically dispersed in THF for 30 min. The obtained slurry was printed on titanium current collectors, and the solvent was evaporated at 80 °C under vacuum. The specific capacity was calculated by using the actual weight of active materials (80% weight of total electrode materials for MPB and 70% for MPB/RGO).

3. Results and discussion

Both samples, MPB and MPB/RGO have been employed for the electrochemical characterizations. Fig. 1 shows a comparison of powder XRD patterns of MPB, MPB/RGO and of restacked graphene. The broad peaks of MPB and MPB/RGO are indicative for the nanosized features of the composites, and the broader peaks of MPB/RGO than MPB show that the ball milling process mechanically reduced the particle size further. Both of them show a good agreement with literature pattern of Mn ferrocyanide (cubic, $a = 10.1189(9) \text{ \AA}$, $V = 1036.1 \text{ \AA}^3$) [8]. Due to the coincidence of MPB peaks covering those of restacked graphene and to the low amount of graphene (10%) it is difficult to completely rule out any restacked graphene in MPB/RGO by XRD alone.

Based on C, H, N elemental analysis and ICP investigations the chemical compositions of the composites MPB and MPB/RGO were determined to be K_{1.8}Mn_{1.1}Fe(CN)₆ · 0.5H₂O and 88 wt.% K_{1.8}Mn_{1.1}Fe(CN)₆ · 0.27H₂O/12 wt.% C, respectively. Experimental and calculated compositions are listed in Table 1. Accordingly and consistent with the raw chemicals used for synthesis, the oxidation states of both Mn and Fe are calculated to be +2. After heat treatment at 200 °C under vacuum, the crystal water was reduced from 0.5 to 0.27 per mole MPB, and the initial 20 wt.% of graphene oxide were reduced to 12% of RGO.

Fig. 2 presents TEM images and ED pattern of MPB and MPB/RGO. As shown in Fig. 2a and b, the particle size of MPB ranges between 10 and 20 nm diameters with irregular shapes. In Fig. 2c, lattice plane separations are observed which correspond to the cubic MPB structure (dark heavy contrasts in MPB arise from transition metals Fe,

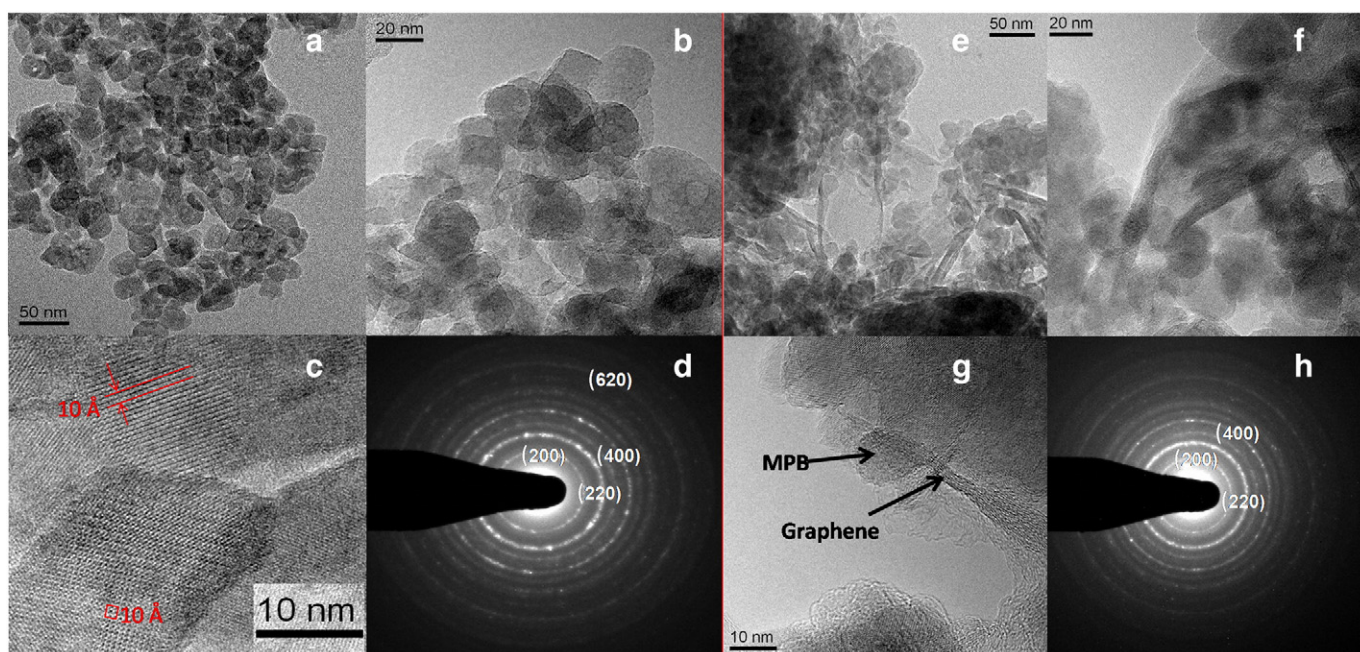


Fig. 2. TEM images of MPB (a, b, c) and MPB/RGO (e, f, g); electron diffraction patterns with *fcc* indexing of MPB (d) and MPB/RGO (h).

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