Bacteria Absorption-Based Mn$_2$P$_2$O$_7$-Carbon @ Reduced Graphene Oxides for High Performance Lithium-Ion Battery Anodes

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As the Mn 3d5 orbit is not fully filled, the spin polarization of Mn$_2$P$_2$O$_7$ should be considered. During the calculation, nonmagnetic (NM), ferromagnetic (FM), ferrimagnetic and antiferromagnetic (AF) cases are taken into account. After optimization for Mn$_2$P$_2$O$_7$ using the density functional theory (DFT), it is found that the AF case has the lowest energy, which indicated that the ground state of Mn$_2$P$_2$O$_7$ should be antiferromagnetic. Thus only the AF case will be discussed below. The Supplementary Table 2 lists the differences between the total energy with spin polarization and without spin polarization $\Delta E$ of Mn$_2$P$_2$O$_7$ as compared with experimental data, and clearly, the AF state is consistent with the experimental findings.$^{51}$ The accuracy of our numerical procedure has been carefully tested. For Mn$_2$P$_2$O$_7$, we obtained lattice parameters that are in good agreement with the experimental values (see Supplementary Table 2).$^{51, S2}$ The error bar which comes from comparing the experimental data from published work for both the theory and experimental data is less than 4%. 

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**Supplementary Table 1.** Single Li atom intercalation energies ($E_i$) and the minimum Li-O distances ($d$).

Labels M1, T, M and B represent the different intercalation sites for Li in Mn$_2$P$_2$O$_7$ (see supplementary Figure 1) with the T site being the most favored site.

<table>
<thead>
<tr>
<th>site</th>
<th>$E_i$ (eV)</th>
<th>$d$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>-1.53</td>
<td>1.97</td>
</tr>
<tr>
<td>T</td>
<td>-1.73</td>
<td>1.92</td>
</tr>
<tr>
<td>M</td>
<td>-1.34</td>
<td>1.99</td>
</tr>
<tr>
<td>B</td>
<td>0.61</td>
<td>1.76</td>
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</tbody>
</table>

**Supplementary Table 2.** Calculated equilibrium lattice parameters ($a$, $b$, and $c$), volume ($V_0$) and the difference between total energy with spin polarization and without spin polarization $\Delta E$ of Mn$_2$P$_2$O$_7$ compared with experimental data.

<table>
<thead>
<tr>
<th></th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$V_0$ (Å$^3$)</th>
<th>$\Delta E$ (eV)</th>
</tr>
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<tbody>
<tr>
<td>NM</td>
<td>6.48</td>
<td>7.97</td>
<td>4.59</td>
<td>233.15</td>
<td>—</td>
</tr>
<tr>
<td>FM</td>
<td>6.71</td>
<td>8.71</td>
<td>4.59</td>
<td>261.76</td>
<td>-10.55</td>
</tr>
<tr>
<td>AF</td>
<td>6.71</td>
<td>8.69</td>
<td>4.60</td>
<td>261.68</td>
<td>-10.60</td>
</tr>
<tr>
<td>Expt. S1</td>
<td>6.60</td>
<td>8.56</td>
<td>4.52</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Expt. S2</td>
<td>6.63</td>
<td>8.58</td>
<td>4.55</td>
<td>252.6</td>
<td>—</td>
</tr>
</tbody>
</table>
Supplementary Figure 1: (a) Schematic illustration of culturing GPBBS, adding the metallic salt (manganese acetate) and washing by centrifuge. (b) Schematic illustration of GPBBS with absorbed metallic Mn$^{2+}$ ions and the formation of Mn$_2$O$_3$P$_7$, and bacterium wall carbonization.

Supplementary Figure 2: Elemental maps of the C, Mn, P, O.

In order to further investigate the presence of Mn, a local elemental map was carried out, as shown in Supplementary Figure 2. The area of the elemental maps of C, Mn, P and O overlap very well, while the area of the elemental map of Mn is slightly smaller compared to that of C, which verifies the uniform distribution of Mn inside the GPBBS but not outside the GPBBS.
Supplementary Figure 3: EDX pattern of the pure bacteria based carbon.

Supplementary Figure 3 shows the EDX microanalysis for the pure bacteria based carbon. The entire nanostructures are found to consist of mainly C, O, P, Si and other metallic elements Ca, Mg, Al, which indicate the element of P come from its nature component.

Supplementary Figure 4: Different intercalation sites (M1, T, M, B) for Li in Mn$_2$P$_2$O$_7$. The top row represents the unit cell geometry before optimization, while the bottom row corresponds to the same after optimization.
Supplementary Figure 5: SEM images of the Mn$_2$P$_2$O$_7$-carbon@RGO paper prepared with (a) Mn$^{2+}$ on the surface of the bacteria were not washed away completely, and (b) Mn$^{2+}$ ions on the surface of the bacteria were washed away completely.

Due to the local negative charge of bacterial surface associated with the polyanionic chains and thick peptidoglycan layer, Mn$^{2+}$ can be absorbed by bacteria through metabolic process. However, some Mn$^{2+}$ might be also adhere onto the bacterial surface through electrostatic interaction, so it is necessary to centrifuge to wash away the Mn$^{2+}$ ions which adhered on surface of the bacteria (as mentioned in the Methods section). The trace amount of Mn$^{2+}$ ions on the surface of the bacteria that did not wash away completely resulted in the formation of MnO$_X$ nanoparticles on the outer surface of the bacteria (see upper SEM image of Supplementary Figure 5). On the other hand, when the Mn$^{2+}$ ions on the outer surface of the bacteria are washed away completely, the outer surface of the bacteria appears smooth (see under SEM image of Supplementary Figure 5).

Supplementary Figure 6: SEM images of the pure Gram-positive Bacteria Bacillus Subtilis (GPBBS).
Supplementary Figure 7: Raman spectrum of the RGO (a) and Mn$_2$P$_2$O$_7$–carbon @ RGO paper (b). In spectra, the D peak and G peak correspond to the disorder-induce D band and the graphitic G band. Additional peaks present in (b) correspond to Mn$_2$P$_2$O$_7$ peaks.

Supplementary Figure 8: Electrochemical performance of pure GPBBS carbon on RGO paper. (a) Charge and discharge curves measured for a current density of 100 mA g$^{-1}$ at the 1$^{st}$, 2$^{nd}$, 5$^{th}$, and 10$^{th}$ cycles. (b) Capacity measured at increasing current density, and coulombic efficiency plotted as a function of cycle number, the blue points correspond to the charging cycle and the red to the discharge cycle.

Supplementary Figure 9: Electrochemical performance of Mn$_2$P$_2$O$_7$–carbon @ RGO paper. Capacity and coulombic efficiency plotted as a function of cycle number for a current density of 1000 mA g$^{-1}$.

The cycle performance of the electrode Mn$_2$P$_2$O$_7$–carbon @ RGO paper was characterized in 0.01 – 3.0 V voltage range at a current density of 1000 mA g$^{-1}$ over 200 cycles. It is noteworthy that the electrode
Mn$_2$P$_2$O$_7$–carbon @ RGO paper exhibits a high capacity even with ultrahigh current density. As shown in Supplementary Fig. 9, the first specific charge and discharge capacity of the Mn$_2$P$_2$O$_7$–carbon @ RGO paper are 840.9 and 1131.9 mA h g$^{-1}$ respectively, corresponding to an initial coulombic efficiency of 74.3%. With increasing number of the cycles, the coulombic efficiency of the material increases quickly, and stabilizes quickly around 99.5%. It exhibits a high discharge capacities of 565.83, 585.4, 595.4, 581.4, 594.5 and 579 mA h g$^{-1}$ in the 10th, 20th, 50th, 100th, 150th and 200th cycles, respectively. This experimental observation is attributed to the synergistic reaction of Mn$^{2+}$ containing bacteria with RGO.

**Supplementary Figure 10:** TGA data of the GO (a), bacteria based carbon @ RGO (b) and Mn$_2$P$_2$O$_7$–carbon @ RGO paper in air (c).

**Supplementary Figure 11:** In situ x-ray diffraction pattern of the Mn$_2$P$_2$O$_7$–carbon @ RGO paper charged/discharged to different charging capacity from 5-80 degrees.

As shown in **Supplementary Figure 11**, there are several x-ray diffraction peaks of the
Mn$_2$P$_2$O$_7$–carbon @ RGO paper changing from 35-46 degrees during the course of charged/discharge, which show the Mn$_2$P$_2$O$_7$ Bragg peaks at (131), (131) and (221).

**Supplementary Figure 12:** The relationship between the thickness and capacity of the Mn$_2$P$_2$O$_7$–carbon @ RGO paper.

A series of experiment were carried out in order to find the relationship between the thickness and capacity of the Mn$_2$P$_2$O$_7$–carbon @ RGO paper anode, the result showed that there is no clear difference in capacity with different thickness (see Supplementary Fig. 12).

**Supplementary Figure 13:** Comparison of the discharge capacity of our Mn$_2$P$_2$O$_7$–carbon @ RGO paper and MnO$_2$- bacteria based carbon@RGO paper. All the preparation method is same except only Mn$^{2+}$ ions not absorption by bacteria.
Supplementary Figure 14: Comparison of the electrochemical impedance spectra (EIS) before and after cycling for the Mn$_2$P$_2$O$_7$–carbon @ RGO paper.

The EIS of the Mn$_2$P$_2$O$_7$–carbon @ RGO paper before cycling and after cycling were measured (see Supplementary Fig. 14). The diameter of the semicircle in the high-medium frequency region is bigger compared to the corresponding data obtained on the same paper after cycling, suggesting that the internal resistance before cycling was greater than that after cycling.

Supplementary Fig 15: TEM image shows pristine GPBBS (not containing Mn$^{2+}$) does not reveal the presence of dots inside the cell wall. Confirming that the dots observed in Figure 2 (j) are Mn$_2$P$_2$O$_7$ which result from the assembly of several Mn$_2$P$_2$O$_7$ nanoparticles.
Supplementary Fig 16: The discharge curve of a plane pouch cell at the 150th cycle is shown by the black trace. Next, the pouch cell was bent along its length and the red and blue traces represent its response at the 152nd and 154th cycle. Finally, the pouch cell was bent along its width and its response at the 156th cycle is represented by the green trace. Clearly, there is negligible change between all traces shown in the figure suggesting that the pouch cell is robust.

REFERENCES:

