Insights on the intercalation mechanism of WSe$_2$ onions toward metal ion capacitors: Sodium rivals Lithium

Yichun Wang$^{a,b}$, Xin Zhang$^{a,b}$, Peixun Xiong$^c$, Fuxing Yin$^{a,b}$, Yunhua Xu$^c$, Biao Wan$^{d,e}$, Qingzhou Wang$^{a,b}$, Gongkai Wang$^{a,b,*}$, Puguang Ji$^{a,b,*}$, Huiyang Gou$^e$

$^a$ School of Material Science and Engineering, Research Institute for Energy Equipment Materials, Hebei University of Technology, Tianjin, 300130, China

$^b$ Tianjin Key Laboratory of Materials Laminating Fabrication and Interface Control Technology, Tianjin 300130, China

$^c$ School of Materials Science and Engineering, Key Laboratory of Advanced Ceramics and Machining Technology (Ministry of Education), Tianjin Key Laboratory of Composite and Functional Materials and Tianjin Key Laboratory of Molecular Optoelectronic Science, Tianjin University, Tianjin 300072, China.

$^d$ Key Laboratory of Metastable Materials Science and Technology, College of Material Science and Engineering, Yanshan University, Qinhuangdao 066004, China

$^e$ Center for High Pressure Science and Technology Advanced Research, Beijing 100094, China

*Corresponding authors.

E-mail addresses:

wang.gongkai@hebut.edu.cn (G. K. Wang), jipuguang@hebut.edu.cn (P. G. Ji),
huiyang.gou@hpstar.ac.cn (H. Y. Gou)

▼These authors contributed equally to this work.
Fig. S1. Schematic illustration of the home-made CVD method for synthesis of WSe$_2$.

Fig. S2. XPS large survey spectrum of WSe$_2$. 
Fig. S3. Cyclic stability of WSe$_2$ vs (a) Lithium and (c) Sodium, and Nyquist plots of WSe$_2$ vs (b) Lithium and (d) Sodium.
Fig. S4. (a) and (b) SEM images of commercial WSe$_2$, corresponding rate performances (c) vs Lithium and (d) vs Sodium.

Fig. S5. (a) CV curve of WSe$_2$ vs Lithium at the scan rate of 1 mV s$^{-1}$, (b) CV curve of WSe$_2$ vs Sodium at scan rates of 1 mV s$^{-1}$, and corresponding capacitive contribution (blue region).
Fig. S6 Mechanism analysis of lithiation/delithiation. (a) The initial two discharge/charge curves. The numbers of one to ten refer to different potential stages corresponding to ex situ XRD patterns, and ex situ Raman spectra, (b) ex situ XRD patterns, (c) ex situ Raman spectra collected at the points of one, nine and ten.

As shown in the XRD patterns (Fig. S6a, b), at the OCV state, characteristic peaks of WSe$_2$ can be observed, during the initial charge process, peaks of WSe$_2$ disappear gradually, new diffraction peaks are assigned to the phase of Li$_2$Se. After the discharge process, characteristic peaks corresponding to WSe$_2$ can be identified again (point six and seven), indicating the recovery of WSe$_2$ phase. Subsequently, during the next charge/discharge cycle, the phase of Li$_2$Se still can be identified, indicating the reversible reaction of WSe$_2$ with lithium ion, while, no obvious peaks can be observed at the end of the charge process, indicating very fine structure or even amorphous phase of WSe$_2$ that can not be detected by XRD was obtained (The characteristic peak of WSe$_2$ can be identified at the point of ten in the Raman spectra in Fig.S6c, proving the recovery of WSe$_2$ phase). These results reveal that WSe$_2$ exhibits a reversible reaction with lithium ion, namely, WSe$_2$ + 4Li$^+$ + 4e$^-$ $\leftrightarrow$ W + 2Li$_2$Se. Specifically, during the discharge process, lithium ion intercalates with WSe$_2$, forming Li$_x$Se and W, where W is embedded in the Li$_2$Se matrix, namely Li$_x$WSe$_2$. Subsequently, during the charge process, lithium ion is extracted from the Li$_x$WSe$_2$ and the WSe$_2$ is recovered reversibly. It is worth noting that the electrochemical reaction proceeds accompany with structure refinement or amorphous phase transition of WSe$_2$, consistent with the previous report.$^3$
Fig. S7. *Ex situ* XRD patterns of OCV WSe$_2$ and the preservative film.
Fig. S8 SEM images of electrodes after cycles. (a, b) OCV state, (c, d) lithium ion cell, (e, f) sodium ion cell.

After the charge/discharge process, the morphology of the electrode vs sodium ion did not change a lot as compared with that at the OCV state, except the thin SEI film covered on the WSe$_2$ nanoparticles uniformly. Whereas, very dense SEI film with microstructure can
be observed obviously on the WSe$_2$ onions. These results also support the better performance of WSe$_2$ vs sodium ion than that vs lithium ion.

Fig. S9. Diffusion rate of lithium and sodium ion through the electrode.

Fig. S10. (a) The calculated convex hull of Li$_x$(WSe$_2$)$_{1-x}$ for obtained candidates within the structural searching, the phases on the lines indicate its thermodynamic stability, (b) the structures of relatively stable phases of Li$_{3.667}$WSe$_2$ and Li$_6$WSe$_2$ as compared with Na$_x$(WSe$_2$)$_{1-x}$, in which the very different configurations can be observed, (c) the global
energy comparison of Li$_{3.667}$WSe$_2$ and Li$_6$WSe$_2$ with different constituent elements/compounds.
Fig. S11. (a) Schematic illustration of lithiation/delithiation mechanism, (b) CV curves and (c) galvanostatic charge/discharge profiles of LICs, (d) Ragone plots of LICs full cell based on WSe$_2$ anode and AC cathode, (e) cyclic stability of LICs full cell at a current density of 1000 mA h g$^{-1}$. 

Intercalation Reaction: $\text{WSe}_2 + 4\text{Li}^+ + 4\text{e}^- \leftrightarrow \text{W} + 2\text{Li}_2\text{Se}$
Fig. S12. (a) CV curves of SICs at various potential windows, and (b) specific capacitance at various current densities.
Table S1 Comparison of electrochemical properties with previous reports for Sodium ion anode.

<table>
<thead>
<tr>
<th>Active material</th>
<th>Preparation</th>
<th>Initial coulombic efficiency</th>
<th>Reversible specific capacity</th>
<th>Rate performance</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>WSe$_2$/C composites</td>
<td>high energy ball milling</td>
<td>58.5 %</td>
<td>294 mAh g$^{-1}$ at 1 A g$^{-1}$</td>
<td>208 mAh g$^{-1}$ at 1 A g$^{-1}$</td>
<td>1</td>
</tr>
<tr>
<td>Bulk WSe$_2$</td>
<td>Commercial</td>
<td>57.3 %</td>
<td>228 mAh g$^{-1}$ at 0.02 A g$^{-1}$</td>
<td>130 mAh g$^{-1}$ at 0.4 A g$^{-1}$</td>
<td>2</td>
</tr>
<tr>
<td>WSe$_2$ nanoplates</td>
<td>Solid-phase synthesis one-step solvothermal process</td>
<td>60.3 %</td>
<td>450 mAh g$^{-1}$ at 0.1 A g$^{-1}$</td>
<td>322 mAh g$^{-1}$ at 0.8 A g$^{-1}$</td>
<td>3</td>
</tr>
<tr>
<td>MoO$_2$/MoSe$_2$-graphene</td>
<td>CVD</td>
<td>81%</td>
<td>404 mAh g$^{-1}$ at 0.1 A g$^{-1}$</td>
<td>301 mAh g$^{-1}$ at 3.2 A g$^{-1}$</td>
<td>4</td>
</tr>
<tr>
<td>WSe$_2$ onions</td>
<td></td>
<td>81.9%</td>
<td>403 mAh g$^{-1}$ at 0.1 A g$^{-1}$</td>
<td>309 mAh g$^{-1}$ at 3.2 A g$^{-1}$</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>330 mAh g$^{-1}$ at 0.8 A g$^{-1}$</td>
<td>214 mAh g$^{-1}$ at 10 A g$^{-1}$</td>
<td></td>
</tr>
</tbody>
</table>

References


Table S2 Bonding strength of W-W pairs of various compounds.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>W-W bond length (Å)</th>
<th>-ICOHP(eV/pair)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂WSe₂</td>
<td>2.46</td>
<td>3.60</td>
</tr>
<tr>
<td>Na₃.₇₅WSe₂</td>
<td>2.31</td>
<td>4.73</td>
</tr>
<tr>
<td>Li₃.₆₆₇WSe₂</td>
<td>2.57</td>
<td>3.02</td>
</tr>
<tr>
<td>Li₆WSe₂</td>
<td>2.49</td>
<td>3.30</td>
</tr>
</tbody>
</table>