

**Supporting Information**

**Reversible conversion reaction of GeO<sub>2</sub> boost lithium-ion storage via Fe doping**

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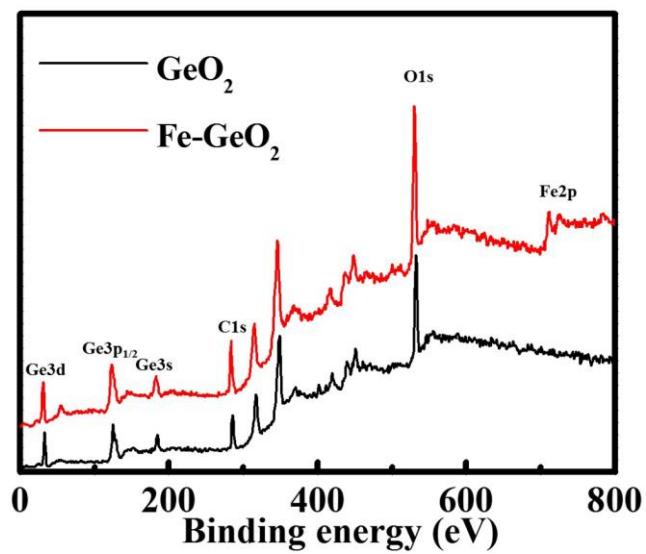
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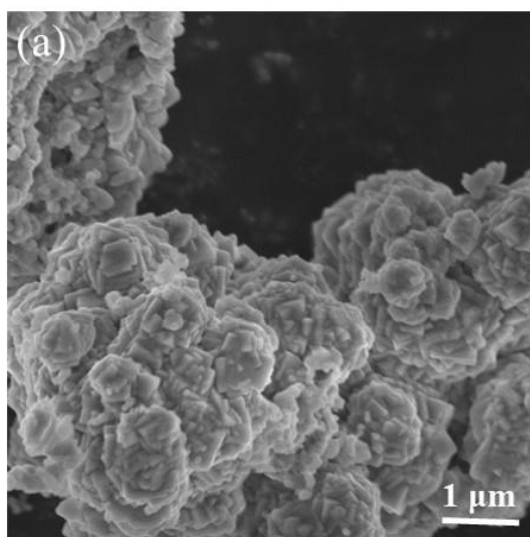
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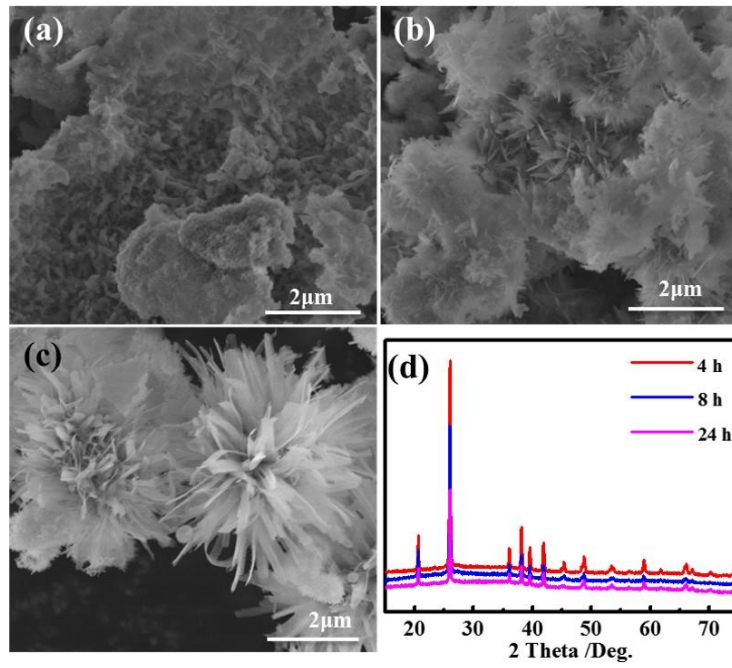
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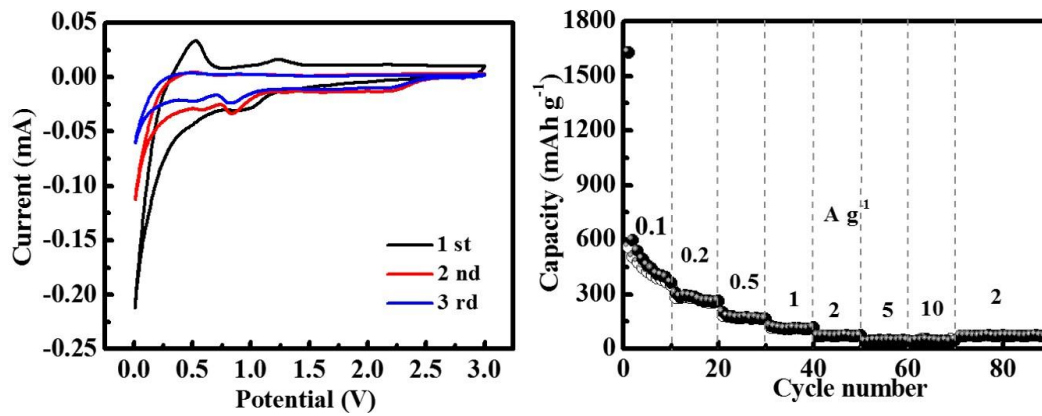
**Fig. S1.** XPS spectra of  $\text{Fe-GeO}_2$  and  $\text{GeO}_2$ , respectively.



**Fig. S2.** SEM image of  $\text{GeO}_2$ .



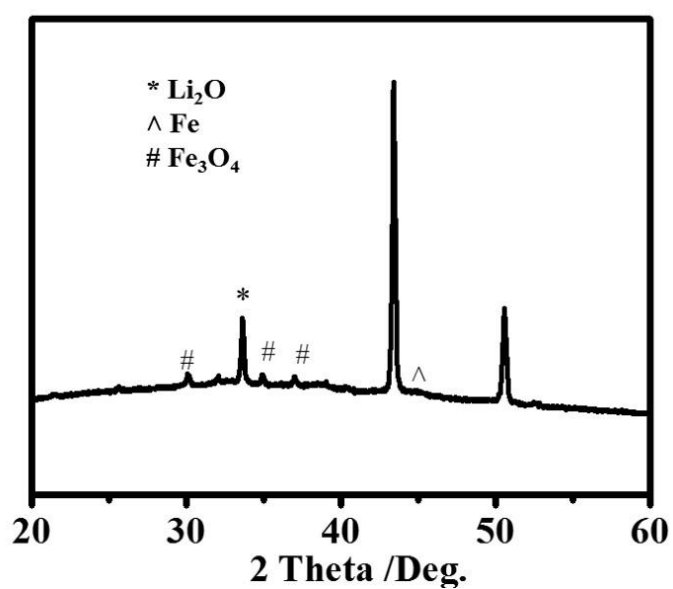
**Fig. S3.** (a-c) SEM images and (d) XRD patterns of Fe-GeO<sub>2</sub> with different reaction times: 4h, 24h and 72h.



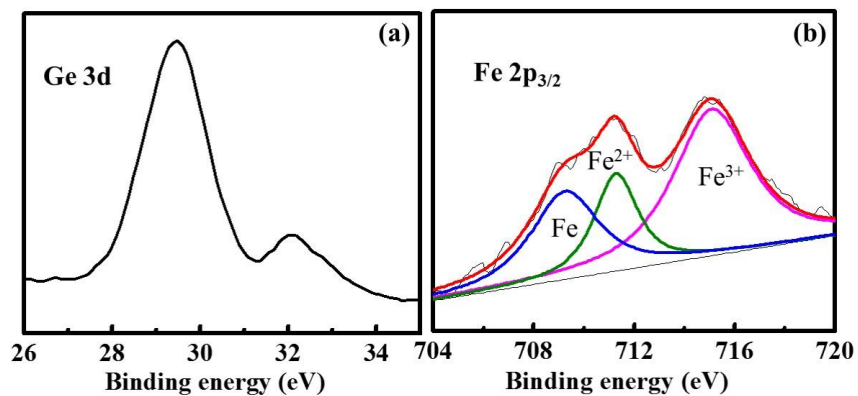
**Fig. S4.** (a) CV curves with a scan rate of 0.3 mV s<sup>-1</sup> and (b) rate capabilities from 0.1 to 10 A g<sup>-1</sup> for GeO<sub>2</sub>.

**Table S1.** Comparison of electrochemical properties of GeO<sub>2</sub> anodes.

Materials	current density/ mA h g <sup>-1</sup>	capacity	cycles	voltage range
GeO <sub>2</sub> /N-C <sup>1</sup>	560	905	300	0.01~1.5
GeO <sub>x</sub> sandwich nanoflakes <sup>2</sup>	333	1008	200	0.01-1.2
crystalline GeO <sub>2</sub> IO <sup>3</sup>	300	521	1000	0.01-1.5
Ge-Fe-OxNWs <sup>4</sup>	100	750	50	0.01-3.0
GeO <sub>2</sub> /C <sup>5</sup>	500	914	400	0.01-1.5
GeO <sub>2</sub> /Graphen <sup>6</sup>	200	1012	50	0.01-1.5
germanium oxide@GO <sup>7</sup>	250	1000	50	0.01-2.5
<b>this work</b>	<b>1000</b>	<b>866</b>	<b>1000</b>	<b>0.01-3.0</b>

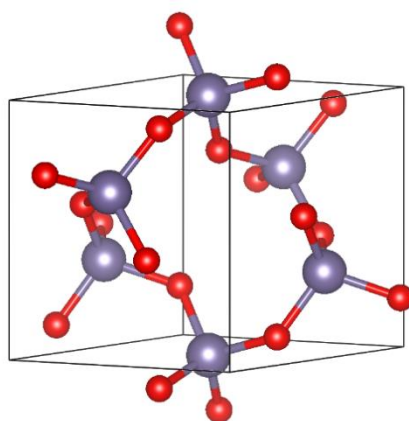


**Fig. S5.** XRD pattern of Fe-GeO<sub>2</sub> electrode after 1000 cycles

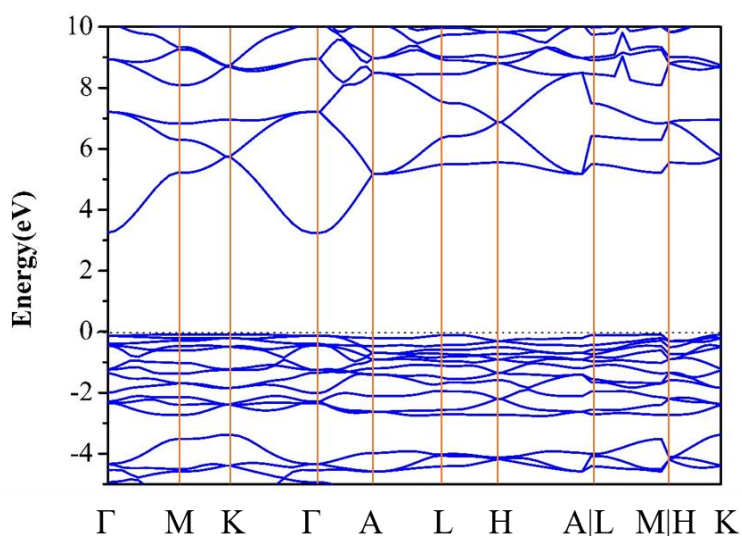


**Fig. S6.** High-resolution XPS spectra for (a) Ge 3d, and (b) Fe 2p of Fe-GeO<sub>2</sub> electrode after 1000 cycles.

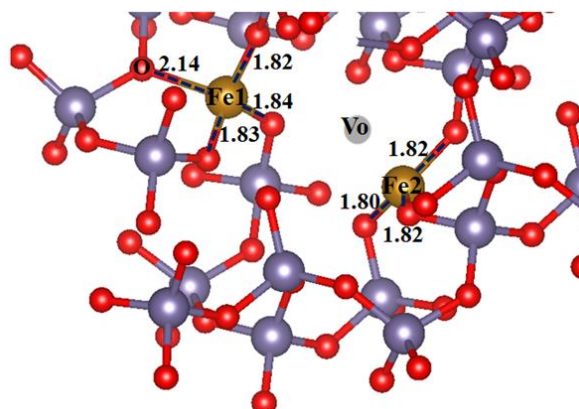
The space group of GeO<sub>2</sub> is P3<sub>1</sub>21, belonging to hexagonal crystal system (Fig. S7). The lattice parameters optimized by PBE were 4.945 Å for *a* and *b*, and 5.679 Å for *c*, which is more close to experiment result comparing with previous theoretical study.<sup>8</sup>



**Fig. S7.** Conventional unit cell of GeO<sub>2</sub>. (Ge atoms are in purple and O atoms are in red).

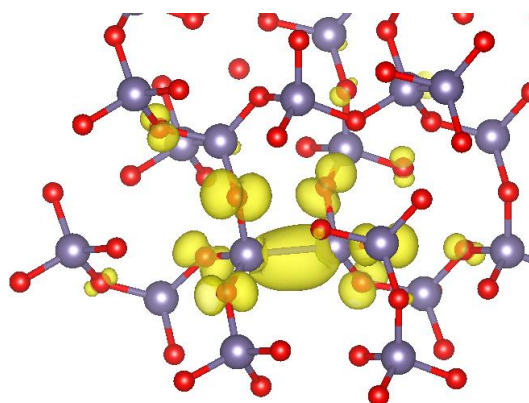


**Fig. S8.** Calculated band structure of  $\text{GeO}_2$  by GGA-PBE.  $\Gamma$  (0.000 0.000 0.000), M (0.500 0.000 0.000), K (0.333 0.333 0.000), A (0.000 0.000 0.500), L (0.500 0.000 0.500), H (0.333 0.333 0.500).<sup>9</sup>

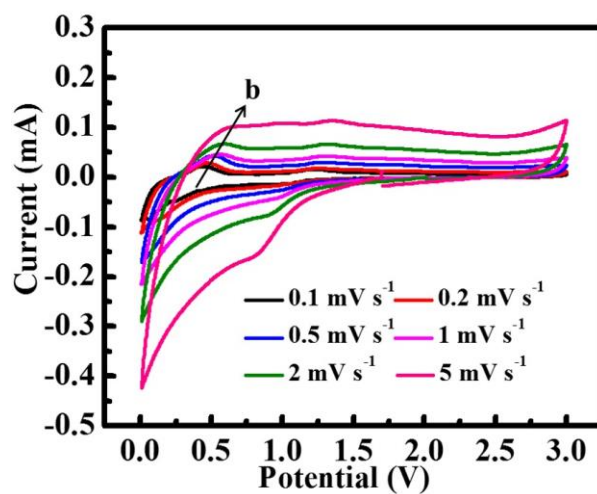


**Fig. S9.** The most stable configuration of  $\text{Fe-GeO}_2$ . The Fe-O distances are in Å. Purple, red, yellow, and grey spheres represent Ge, O, Fe atoms and oxygen vacancy, respectively.

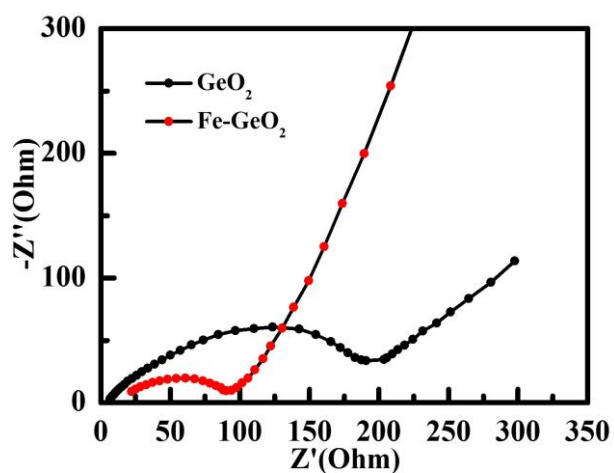
For the  $\text{Fe}^{3+}$  doping, we considered all possible configurations by replacing two Ge species with two iron atoms and removing one oxygen atom for charge compensation. The most stable configuration is shown in Fig. S8, in which the two iron prefer to stay close and the oxygen vacancy is linked by the two iron. After the relaxation, the initial threefold coordinated Fe1 has four bonds with nearest oxygen (lengths are 1.82, 1.83, 1.84 and 2.14 Å). The ligancy of one of the oxygens connected Fe1 changed from two into three. The Fe2 still maintains initial ligancy (Fe-O bond lengths are 1.80, 1.82 and 1.82 Å). The reason we think for this most stable configuration is the structure optimized can still maintain the Ge four fold coordination in  $\text{GeO}_2$  and the minimum re-arranged bonds, which is consistent with the previous study about trivalent atoms as dopant in  $\text{GeO}_2$ .<sup>10</sup> For the most stable configuration, we find that AFM is the most stable spin state, which matches with experiment result at room temperature.



**Fig. S10.** The Highest occupied orbital at Gamma point of  $2 \times 2 \times 2$   $\text{GeO}_2$  with one oxygen vacancy.



**Fig. S11.** CV curves at different scan rates from 0.1 to  $5 \text{ mV s}^{-1}$  of  $\text{GeO}_2$ .



**Fig. S12.** EIS measurements for  $\text{GeO}_2$  and  $\text{Fe-GeO}_2$  after 1000 cycles.

## References

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