Electronic Supplementary Information:

Phase engineering in lead-bismuth system for advanced magnesium ion batteries

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The calculation process of theoretical simulation:
The crystal structure of Mg$_2$Pb was obtained from the PDF card (*Fm-3m* (225), JCPDS no. 65-2998). Owing to the low content of Bi in Mg$_2$(Pb$_{0.85}$Bi$_{0.15}$), the XRD patterns of Mg$_2$(Pb$_{0.85}$Bi$_{0.15}$) may be similar with those of Mg$_2$Pb, suggesting that its crystal structure may be equivalent to that of Mg$_2$Pb. Hence, the crystal structures of Mg$_2$(Pb$_{0.85}$Bi$_{0.15}$) can be established based on the structure of Mg$_2$Pb by substituting Pb atoms by Bi atoms and subsequently relaxed by VASP. Notably, there are four kinds of crystal structures of Mg$_2$(Pb$_{0.85}$Bi$_{0.15}$) due to four possible substituted modes for Bi atoms. The four possible scenarios are as follows: three Bi atoms arranged together (termed as Mg$_2$(Pb$_{0.85}$Bi$_{0.15}$)-a), two Bi atoms arranged together and one separated (termed as Mg$_2$(Pb$_{0.85}$Bi$_{0.15}$)-b), three Bi atoms all separated by Pb (termed as Mg$_2$(Pb$_{0.85}$Bi$_{0.15}$)-c) and Bi atoms randomly distributed (termed as Mg$_2$(Pb$_{0.85}$Bi$_{0.15}$)-random). Furthermore, the simulated XRD patterns were calculated using the four crystal structures of Mg$_2$(Pb$_{0.85}$Bi$_{0.15}$) by the Reflex module in Materials Studio 7.0. Finally, the operando XRD results of the Pb$_{0.7}$Bi$_{0.3}$ electrode after the second discharge are presented for comparison.
Figure S1. Schematic illustration of the operation principle of magnetron co-sputtering method.
Figure S2. Schematic illustration showing the design strategy and preparation process of the Pb-Bi films.
Figure S3. Binary alloy phase diagram of Bi-Pb. The compositions of four kinds of sputtered samples are highlighted.
Figure S4. Macrophotographs of the sputtered Pb$_{0.7}$Bi$_{0.3}$/Bi film showing its flexible, self-supporting and robust feature.
Figure S5. The typical EDX spectra of the sputtered (a) Pb$_{0.7}$Bi$_{0.3}$ and (b) Pb$_{0.7}$Bi$_{0.3}$/Bi films, and the corresponding Pb/Bi elemental contents are shown as insets.
Figure S6. Rietveld refinement results of XRD patterns for the sputtered Pb$_{0.7}$Bi$_{0.3}$/Bi film.
Figure S7. The CV curves of the sputtered (a) Pb, (b) Bi and (c) Pb$_{0.7}$Bi$_{0.3}$ films in the first five cycles at a scan rate of 0.01 mV/s.
Figure S8. The discharge/charge curves of the sputtered (a) Bi, (b) Pb$_{0.7}$Bi$_{0.3}$ and (c) Pb$_{0.7}$Bi$_{0.3}$/Bi films in different cycles at 200 mA/g. (d) Cycling stability of the sputtered biphase Pb$_{0.7}$Bi$_{0.3}$/Bi film at 20 mA/g.
Figure S9. The $dV/dQ$ curves of the sputtered Pb$_{0.7}$Bi$_{0.3}$/Bi during the (a) discharge and (b) charge processes.
Figure S10. The discharge/charge curves of the sputtered (a) Pb, (b) Bi, (c) Pb$_{0.7}$Bi$_{0.3}$ and (d) Pb$_{0.7}$Bi$_{0.3}$/Bi films at different current densities.
Figure S11. (a) GITT curves upon the first cycle of the sputtered Pb$_{0.7}$Bi$_{0.3}$/Bi film. (b) Scheme of a single-step GITT experiment at ~ 0.24 V vs. Mg$^{2+}$/Mg for the Pb$_{0.7}$Bi$_{0.3}$/Bi electrode during the discharge process (current density: 10 mA/g).
Figure S12. The cross-section SEM image showing the thickness of the sputtered (a) Pb$_{0.7}$Bi$_{0.3}$/Bi and (b) Pb$_{0.7}$Bi$_{0.3}$ films.
Figure S13. GITT curve and the calculated diffusion coefficient for Mg$^{2+}$ ions upon the first discharge process of the sputtered Pb$_{0.7}$Bi$_{0.3}$ electrode.
Figure S14. The Nyquist plots of the sputtered pure (a) Pb and (b) Bi films at OCV and after the 1st, 2nd, 5th and 10th cycles.
Figure S15. The atomic structures of (a) Mg$_2$Pb and (b-e) Mg$_2$(Pb$_{0.85}$Bi$_{0.15}$) with different Bi configurations.
Figure S16. The comparison of the simulated XRD patterns calculated from the crystal structures of Figure S15 and the operando XRD results of the Pb_{0.7}Bi_{0.3} electrode after the second discharge.
Figure S17. (a) Typical discharge/charge curves during the initial five cycles of the full cell with 0.5 M Mg(TFSI)$_2$. (b) Typical discharge/charge curves during the initial five cycles of the full cell with 0.4 M APC.