Supporting Information for:

**Insight into the electrochemical behavior of micrometric Bi and Mg₃Bi₂ as performant negative electrodes for Mg batteries**

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Figure S1: SEM pictures collected at different magnification of Bi powder after ball-milling pulverization.
Figure S2: GITT curve obtained from Bi/Mg battery. Potential vs. time insets show the fast relaxation of both alloying and de-alloying process.
Figure S3: Experimental XRD pattern (top) and SEM pictures (bottom) of Mg$_3$Bi$_2$ obtained by mechanochemical synthesis (observed, calculated and difference profile respectively on black dots, red and blue lines; Bragg position on green vertical bars).
Figure S4: Galvanostatic curve and CV of the Mg$_3$Bi$_2$ based electrode obtained at C/10 on self-supported electrode, with red arrows showing the influence of the electrochemical grinding on the potential evolution.
Figure S5: *Operando* XRD characterization of the first charge, discharge and second charge of Mg₃Bi₂/Mg battery.
Figure S6: Evolution of integrated areas of Bi (102) and Mg\textsubscript{3}Bi\textsubscript{2} (102) diffraction peaks collected during the operando XRD characterization.

**Synthesis and electrochemical characterization of the positive electrode material Mo\textsubscript{3}S\textsubscript{4} Chevrel phase.**

The synthesis protocol is adapted following the work of Choi *et al.* (ACS Appl. Mater. Interfaces 2015, 7, 7016). Firstly Cu\textsubscript{1.25}Mo\textsubscript{3}S\textsubscript{4} was from stoichiometric amounts of Cu (99.9%, Alfa Aeasar), MoS\textsubscript{2} (99%, Sigma-Aldrich) and Mo (99.95%, Alfa Aeasar). The mixed powders were ground together in Ar atmosphere with spex high-energy milling for 100 minutes. Then the mixture is heated in alumina crucible in tubular furnace under Ar flow during 24 hours at 1100°C. Routine XRD pattern confirms the formation of the phase with no visible impurity (Figure S7a). Secondly the as-obtained powder immersed in acid solution for Cu removal (typically 6h in 50mL of 6mol/L HCl solution for 1g of Cu\textsubscript{2.5}Mo\textsubscript{6}S\textsubscript{8} powder). The leached powder is then filtered and thoroughly wash with DI water and finally ethanol, and finally allowed to dry for 1 night at 100°C under dynamic vacuum. Routine XRD pattern
(Figure S7b) confirms the Cu removal and therefore the formation of Mo$_3$S$_4$ with refined cell parameters in agreement with the work of Chevrel et al. (Mat. Res. Bull. 1974, 9, 1487). A small residue of MoO$_2$ is observed. For electrode formulation, the Mo$_6$S$_8$ is mixed with carbon black PTFE (60/30/10 wt.%) and pressed with mortar and pestle to form a paste which is further punched in disk. Electrochemical testing are performed are C/100 in half-cell with Mg metal as both negative and counter electrode and organohaloaluminate-based electrolyte. The galvanostatic first cycling presented in Figure S7c completely matches with the pioneering work of Aurbach et al. (Nature 2000, 407, 13).

Figure S7: XRD patterns of (a) Cu$_{1.25}$Mo$_3$S$_4$ and (b) Mo$_3$S$_4$ after Cu removal by acid leaching, and galvanostatic signature of Mo$_3$S$_4$ vs. Mg.
Electrochemical tests with complete Mg-ion battery with $\text{Mg}_3\text{Bi}_2$ as negative and $\text{Mo}_6\text{S}_8$ as positive electrodes.

In the pioneering work of Shao et al. (Nano Letters 2014, 14, 255), there is no detail about the relative amount of each electrodes. Consequently it is difficult to analyze the reported capacity of 60mAh/g. Assuming an ideal complete demagnesiation of $\text{Mg}_3\text{Bi}_2$ and a complete magnesiation of $\text{Mo}_6\text{S}_8$ the two active materials should be implemented in the cell following this equation:

$$\text{Mg}_3\text{Bi}_2 + 3\text{Mo}_3\text{S}_4 \rightarrow 2\text{Bi} + 3\text{MgMo}_3\text{S}_4$$

However as this early stage of the work, it was decided to preferentially set the Mg-containing electrode (i.e. $\text{Mg}_3\text{Bi}_2$) as the deficient one. Therefore the $x$ quantity in the galvanostatic curves refers to the Mg content in $\text{Mg}_3\text{Bi}_2$ (Figures 7 in the article).