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Supporting Information for:

Insight into the electrochemical behavior of micrometric Bi and Mg_3Bi_2 as performant negative electrodes for Mg batteries

F.Murgia, L. Stievano, L. Monconduit and R. Berthelot*

Institut Charles Gerhardt de Montpellier (UMR 5253 CNRS Unité de Montpellier)
Équipe Agrégats Interfaces Matériaux pour l'Énergie
2, Place Eugène Bataillon – CC1502 – 34095 Montpellier cedex 5 (France)
Réseau sur le Stockage Électrochimique de l'Énergie (FR 3459 CNRS)
33, Rue Saint Leu – 80039 Amiens cedex (France)

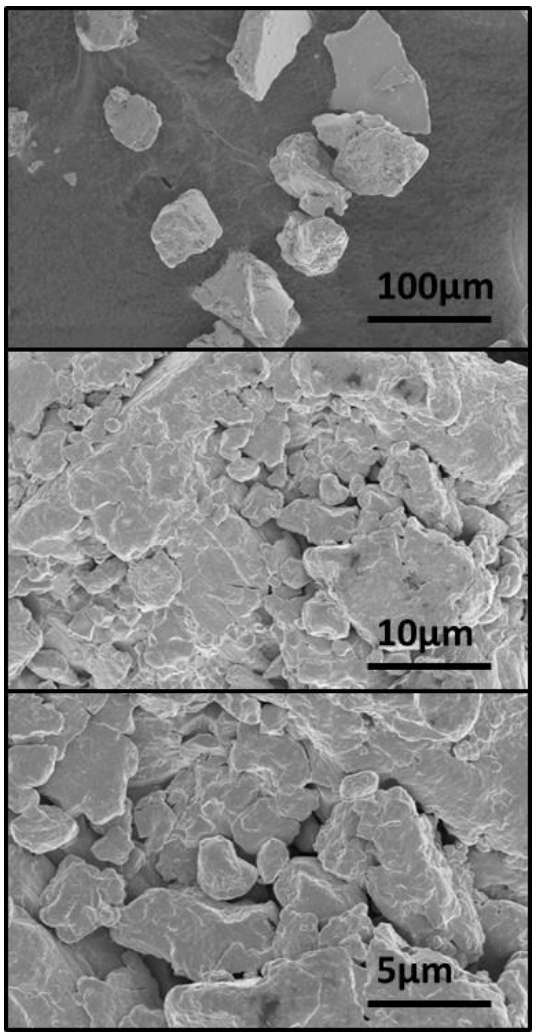

Figure S1: SEM pictures collected at different magnification of Bi powder after ball-milling pulverization.

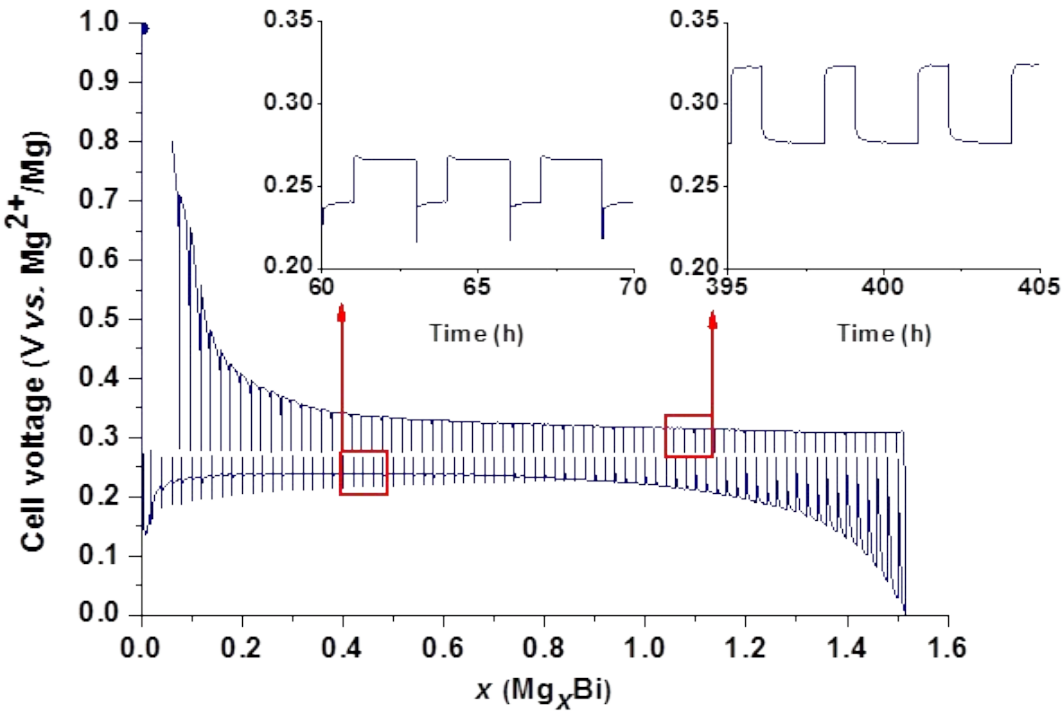

Figure S2: GITT curve obtained from Bi/Mg battery. Potential vs. time insets show the fast relaxation of both alloying and de-alloying process.

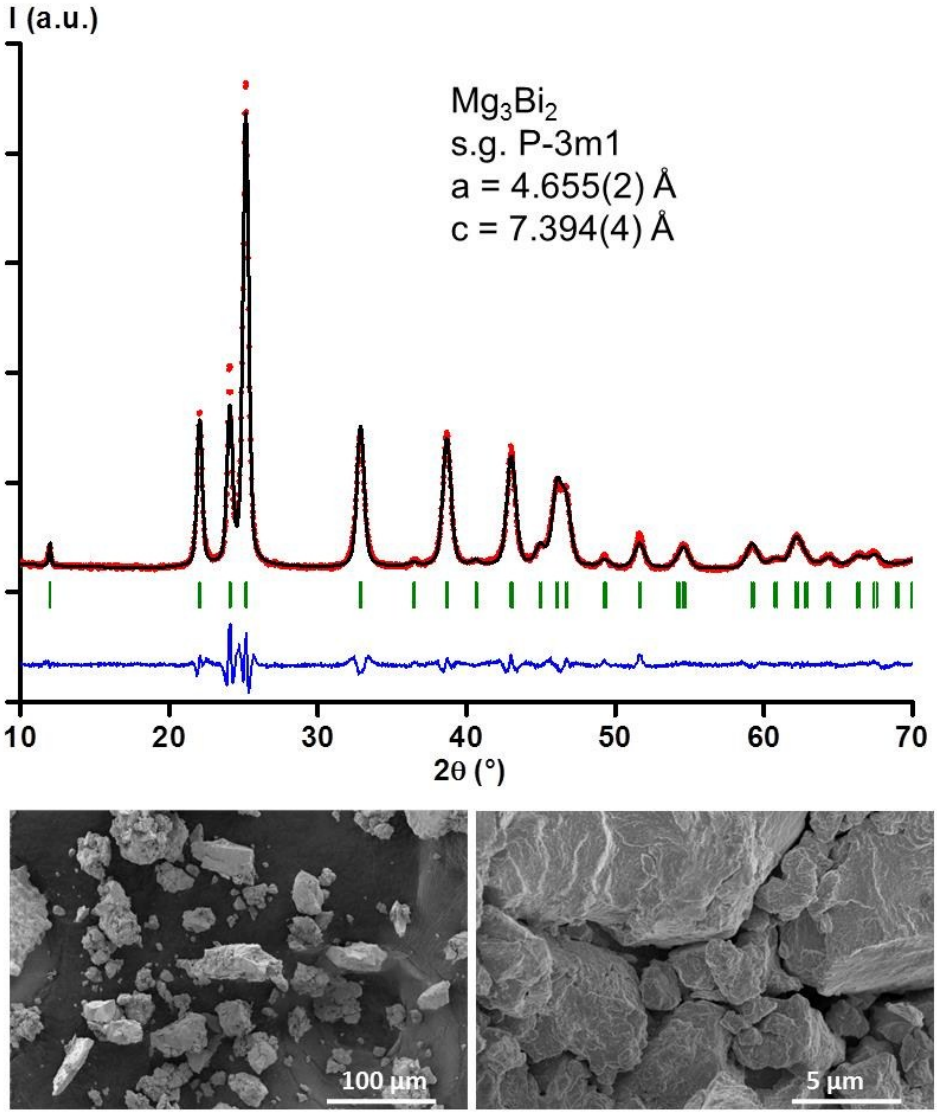

Figure S3: Experimental XRD pattern (top) and SEM pictures (bottom) of Mg_3Bi_2 obtained by mechanochemical synthesis (observed, calculated and difference profile respectively on black dots, red and blue lines; Bragg position on green vertical bars).

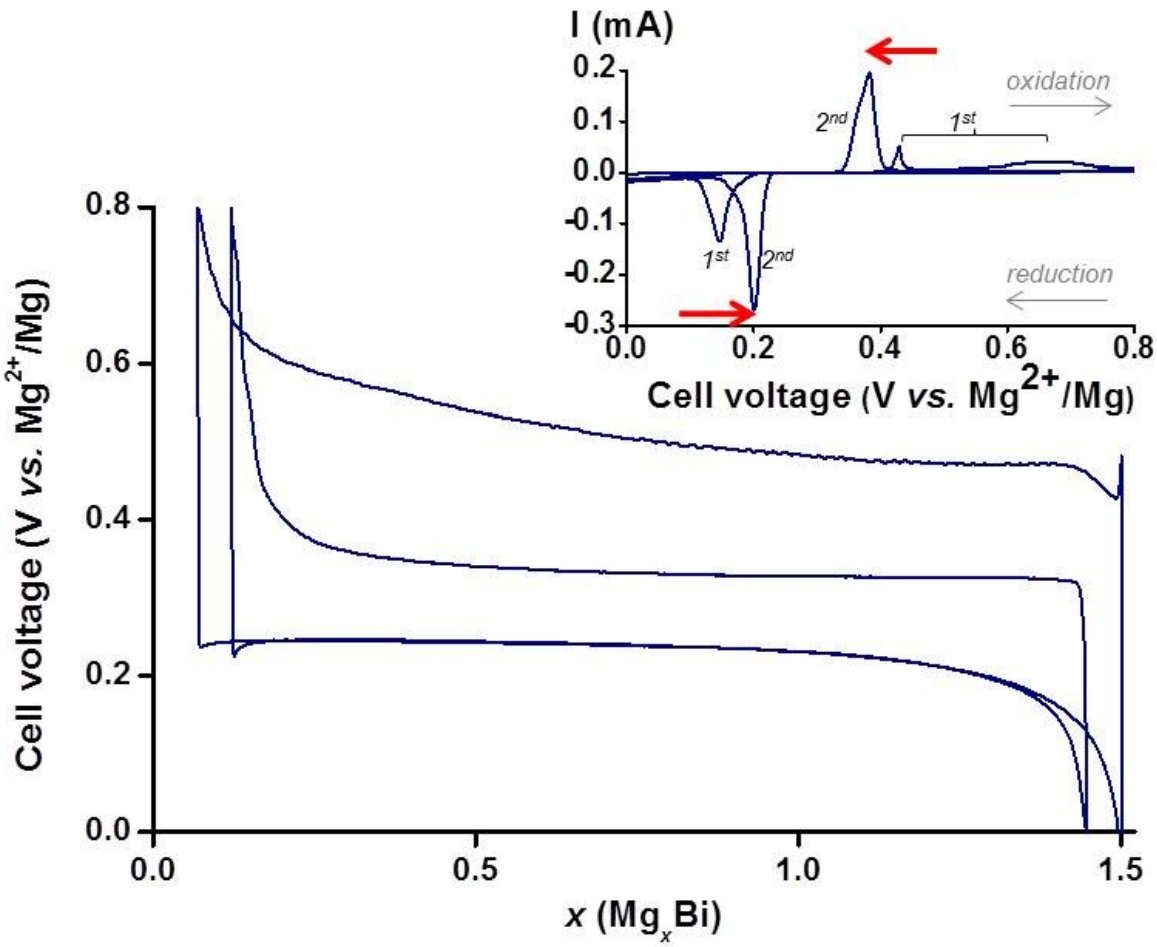

Figure S4: Galvanostatic curve and CV of the Mg_3Bi_2 based electrode obtained at C/10 on self-supported electrode, with red arrows showing the influence of the electrochemical grinding on the potential evolution.

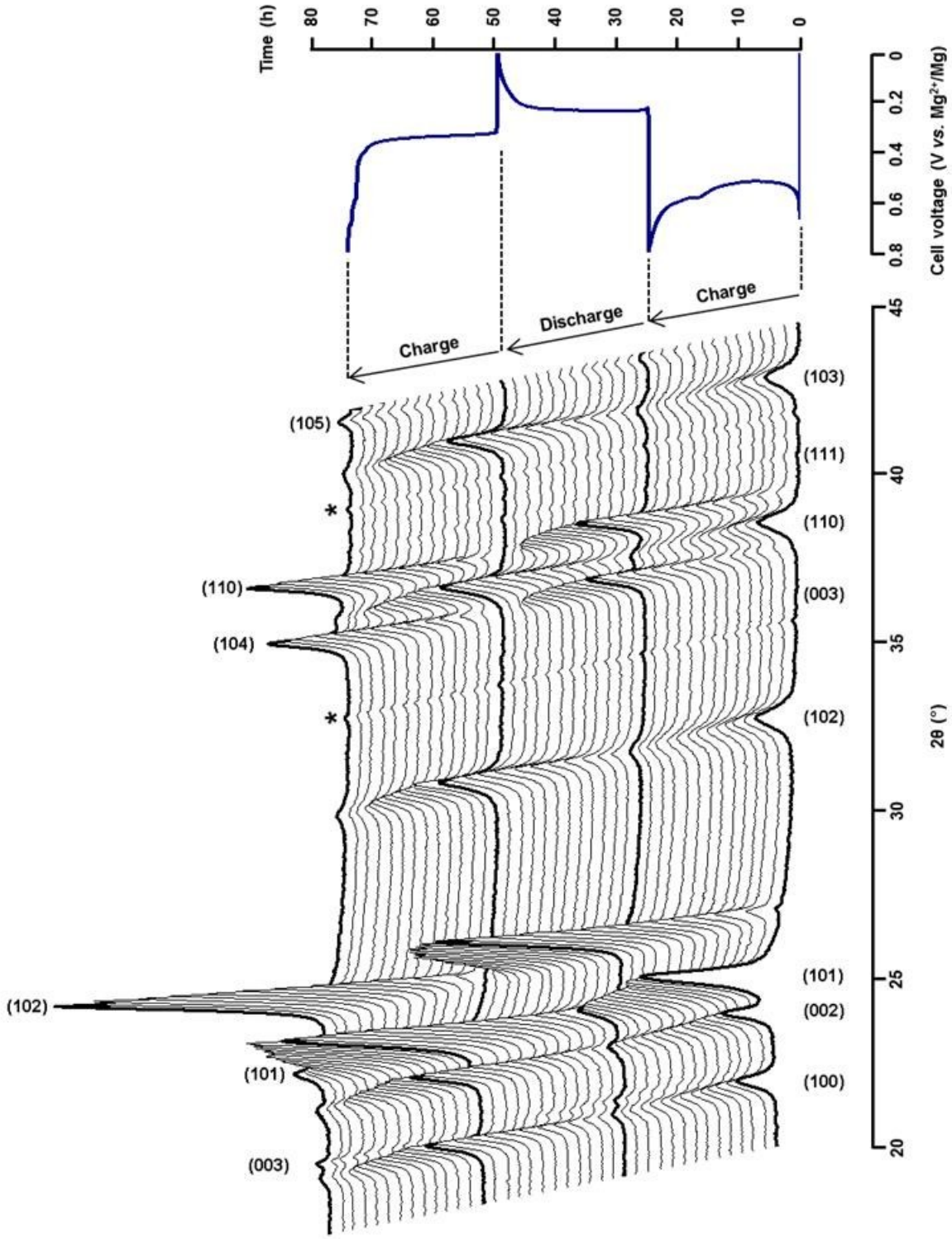

Figure S5: *Operando* XRD characterization of the first charge, discharge and second charge of Mg_3Bi_2/Mg battery.

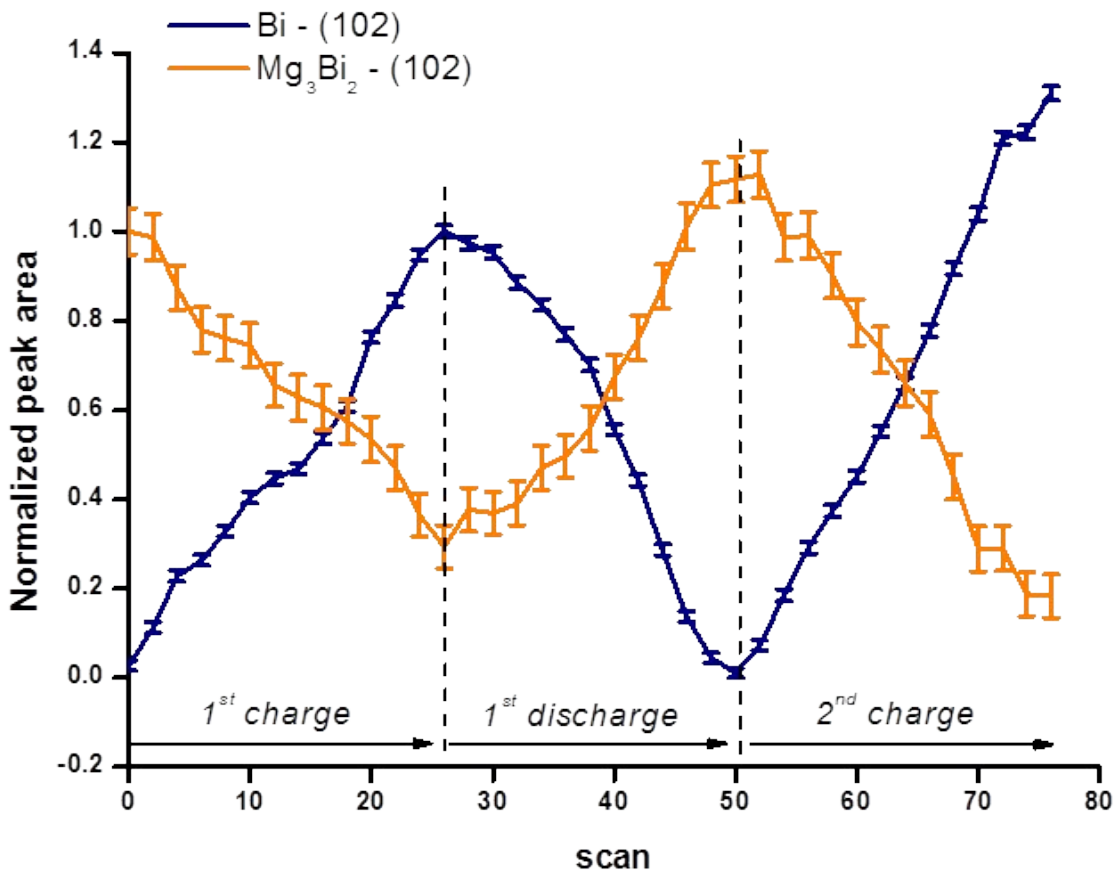

Figure S6: Evolution of integrated areas of Bi (102) and Mg_3Bi_2 (102) diffraction peaks collected during the *operando* XRD characterization.

Synthesis and electrochemical characterization of the positive electrode material Mo_3S_4 Chevrel phase.

The synthesis protocol is adapted following the work of Choi *et al.* (ACS Appl. Mater. Interfaces 2015, 7, 7016). Firstly $Cu_{1.25}Mo_3S_4$ was from stoichiometric amounts of Cu (99.9%, Alfa Aeasar), MoS_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 $Cu_{2.5}Mo_6S_8$ 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_3S_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_6S_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).

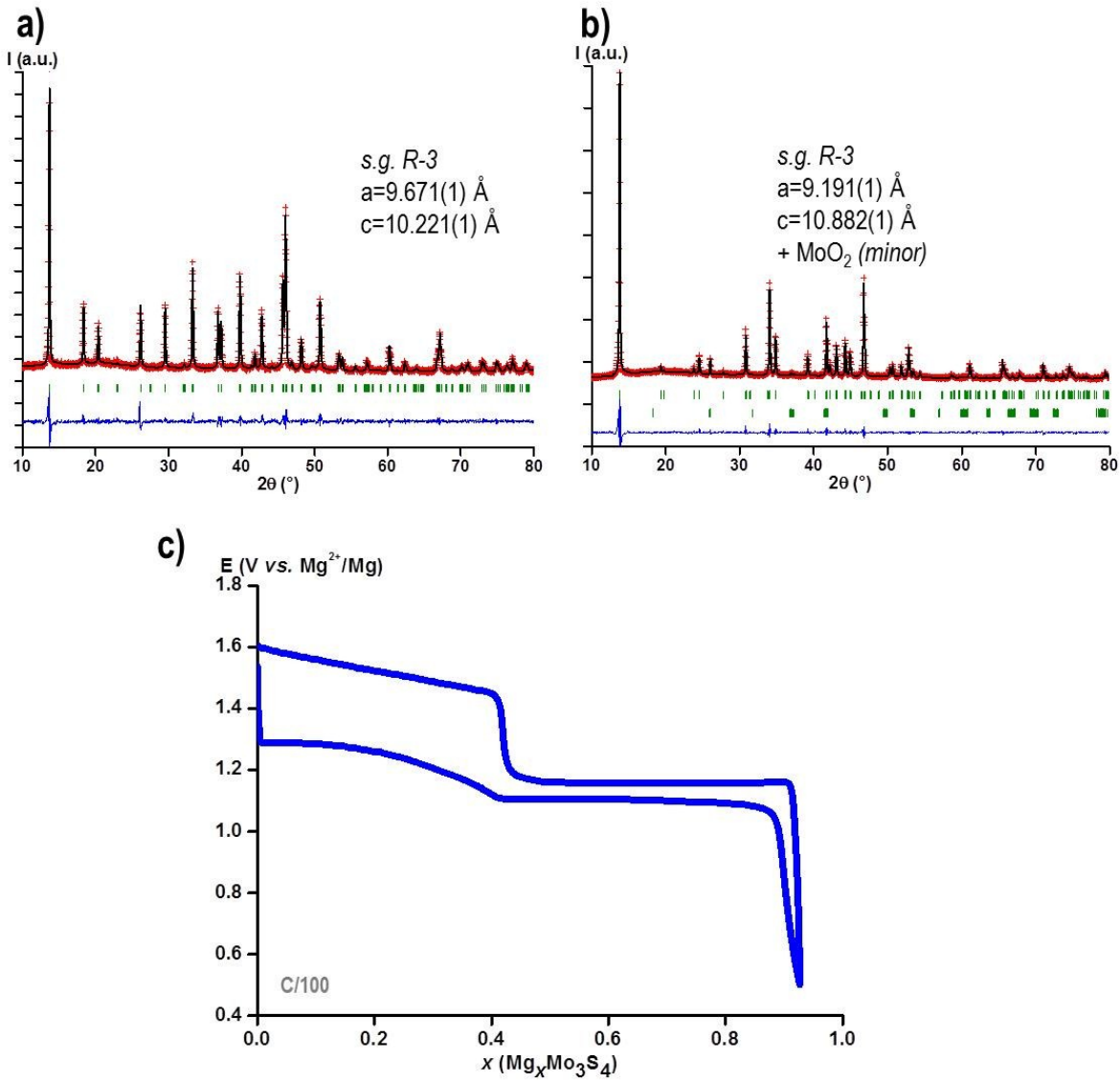

Figure S7: XRD patterns of (a) $Cu_{1.25}Mo_3S_4$ and (b) Mo_3S_4 after Cu removal by acid leaching, and galvanostatic signature of Mo_3S_4 *vs.* Mg.

Electrochemical tests with complete Mg-ion battery with Mg_3Bi_2 as negative and Mo_6S_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 Mg_3Bi_2 and a complete magnesiation of Mo_6S_8 the two active materials should be implemented in the cell following this equation:

$$Mg_3Bi_2 + 3Mo_3S_4 \rightarrow 2Bi + 3MgMo_3S_4$$

However as this early stage of the work, it was decided to preferentially set the Mg-containing electrode (*i.e.* Mg_3Bi_2) as the deficient one. Therefore the *x* quantity in the galvanostatic curves refers to the Mg content in Mg_3Bi_2 (Figures 7 in the article).