Electronic Supplementary Information (ESI) for Energy & Environmental Science



**Supporting Information**

# Body Centered Cubic Magnesium Niobium Hydride with Facile Room Temperature Absorption and Four Weight Percent Reversible Capacity

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## Methods

### Synthesis of Mg-Nb alloys

The binary Mg-Nb alloy films were synthesized by physical vapor deposition (PVD). They were 4 inches in diameter with 150 nm or 1.5 μm thick Mg-based alloy layer. The alloy film was coated with 7.5 nm Pd/7.5 nm Nb bi-layers on the top and bottom of the stack. The Nb interlayer reduced the rate of intermetallic formation between the Mg and the Pd, allowing the Pd to stay catalytically active during the first few cycles[1]. The Pd coating is also effective to prevent the underlying alloy film from oxidation during the transfer/storage before the hydrogen sorption measurement. Deposition was performed using a DC-magnetron co-sputtering system (AJA International Inc. ATC ORION 5), in a sputter-up configuration with continuous substrate rotation. The substrate temperature was maintained near ambient for all depositions. Argon gas with a purity of 99.999% was used at a working pressure of $5 \times 10^{-3}$ mbar, with the maximum base pressure of $5 \times 10^{-8}$ mbar. The Si substrates were first coated with a layer of hardened photoresist to enable post deposition lift-off of the films using acetone. For co-deposition, the Mg sputtering rate was kept at 0.23 nm/s (100 W power). The Nb sputtering rate was adjusted to create the desired stoichiometry.

### Hydrogen Storage Measurement and Microstructural Characterization

Volumetric absorption and desorption kinetic measurements and the desorption pressure-compositions isotherms (PCT-desorption) were performed on an automated Sieverts type hydrogen sorption analysis system (Hy-Energy LLC. PCTPro 2000). The typical sample amount used for each measurement was about 15 milligrams. Absorption was performed at 1 bar hydrogen and room temperature, while desorption was performed at 175 °C and 5 mbar.

X-ray diffraction (XRD) analysis was performed on a Bruker AXS diffractometer (Bruker Discover 8) using a Cu-Kα radiation source (λ = 1.5406Å) that was monochromatized using a single Gobel mirror. The diffractometer was equipped with a HiStar general area 2-dimensional detection system (GADDs) with sample-detector distance of 15 cm. X-ray diffraction analyses were conducted at room temperature. Powder diffraction patterns from both simulated results and XRD database on DIFFRAC$^{plus}$ EVA$^{TM}$ software were used for peak identifications. Scanning electron microscopy (SEM) analysis was performed using a Hitachi field emission

microscope Imaging and selected area electron diffraction (SAD) analysis was performed on JEOL 2100 transmission electron microscope (TEM) operated at 200 kV. This TEM is also equipped with a Gatan imaging filter (GIF). The TEM samples were prepared by directly depositing Mg-Nb alloy films onto ultrathin carbon film supported by a lacey carbon film on a copper grid. Commercial software Desktop Microscopist $^{TM}$ is used to simulate electron diffraction patterns.

**Simulation Method**

The ground state energy calculations ware performed for a 2x2x2 unit cell with Density functional theory (DFT) by using the Vienna ab initio simulation package (VASP)[2]. The core−valence electron interactions were treated using Blöchl's projector-augmented wave (PAW) formalism with a cutoff energy of 300 eV. The optimization of the structural parameters is performed until the forces on the atoms are less than 0.01 eV/Å. The nonlocal exchange and correlation energies were calculated with the Perdew−Wang (PW91) functional within generalized gradient approximation (GGA). The linear tetrahedron method with Blöchl correction[3] is used. Brillouin zone integrations were performed using a Monkhorst−Pack 9 × 9 × 9 *k*-points mesh for best convergence and relaxation to zero strains.

References

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2. G. Kresse, D. Joubert, *Phys. Rev. B* **59**, 1758–1775 (1999).

3. P. E. Blöchl, O. Jepsen, O. K. Andersen, *Phys. Rev. B* **49**, 16223–16233 (1994).

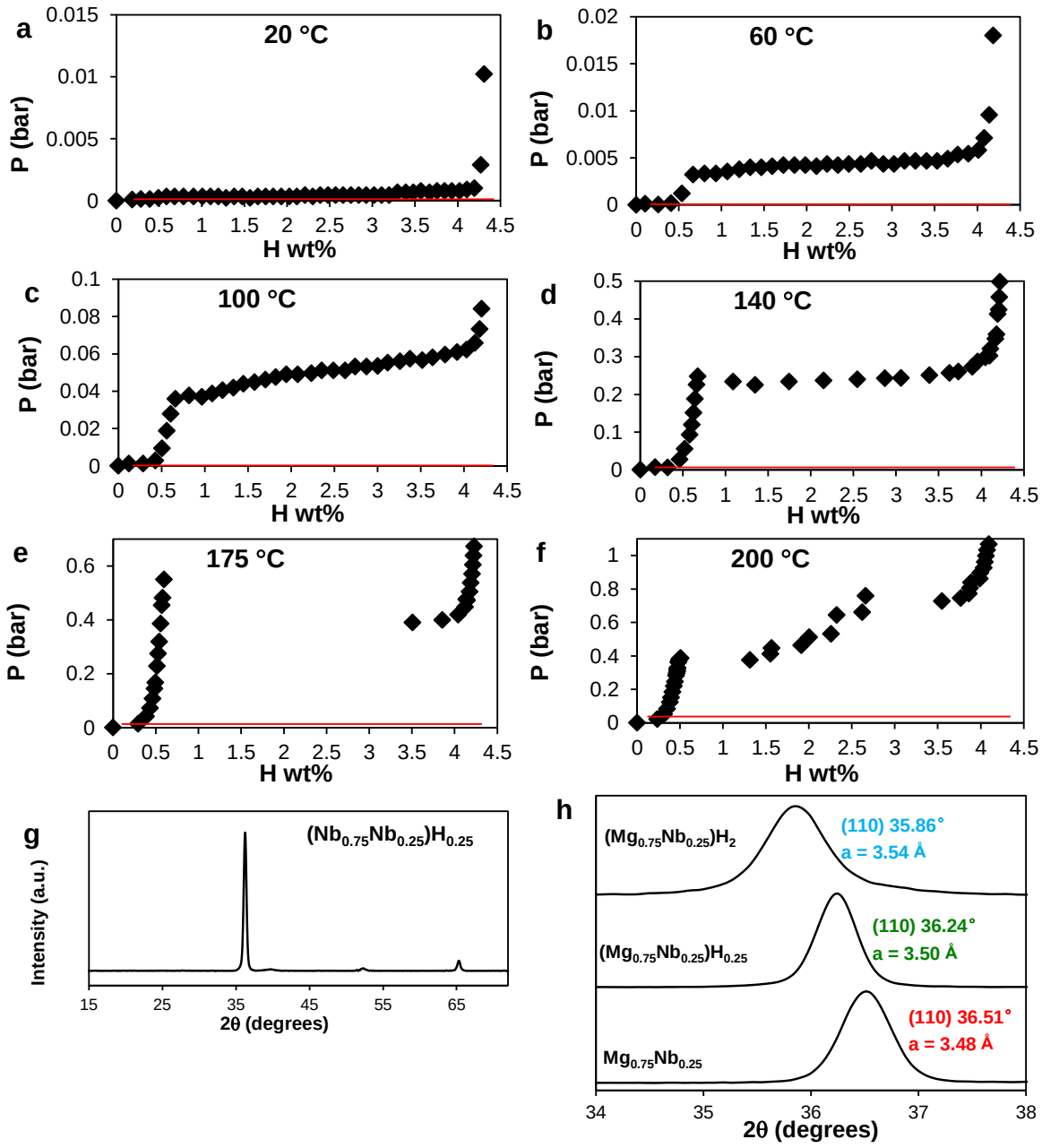


Figure S1. Absorption Pressure-Composites Isotherms of the $Mg_{0.75}Nb_{0.25}$ alloy measured for the first absorption at (a) 20 °C, (b) 60 °C, (c) 100 °C, (d) 140 °C, (e) 175 °C and (f) 200 °C, respectively. All isotherms present two plateau. The higher plateau extends from 0.5 to 4.5 wt.% H, while the lower plateau extends from 0 to 0.5 wt.%. The red line in each graph indicates the expected plateau pressure of $MgH_2$ at corresponding temperature. (g) XRD pattern measured

after the first stage of absorption. (i) The plot of XRD patterns of $Mg_{0.75}Nb_{0.25}$ in as-deposited, partially absorbed and fully absorbed states.

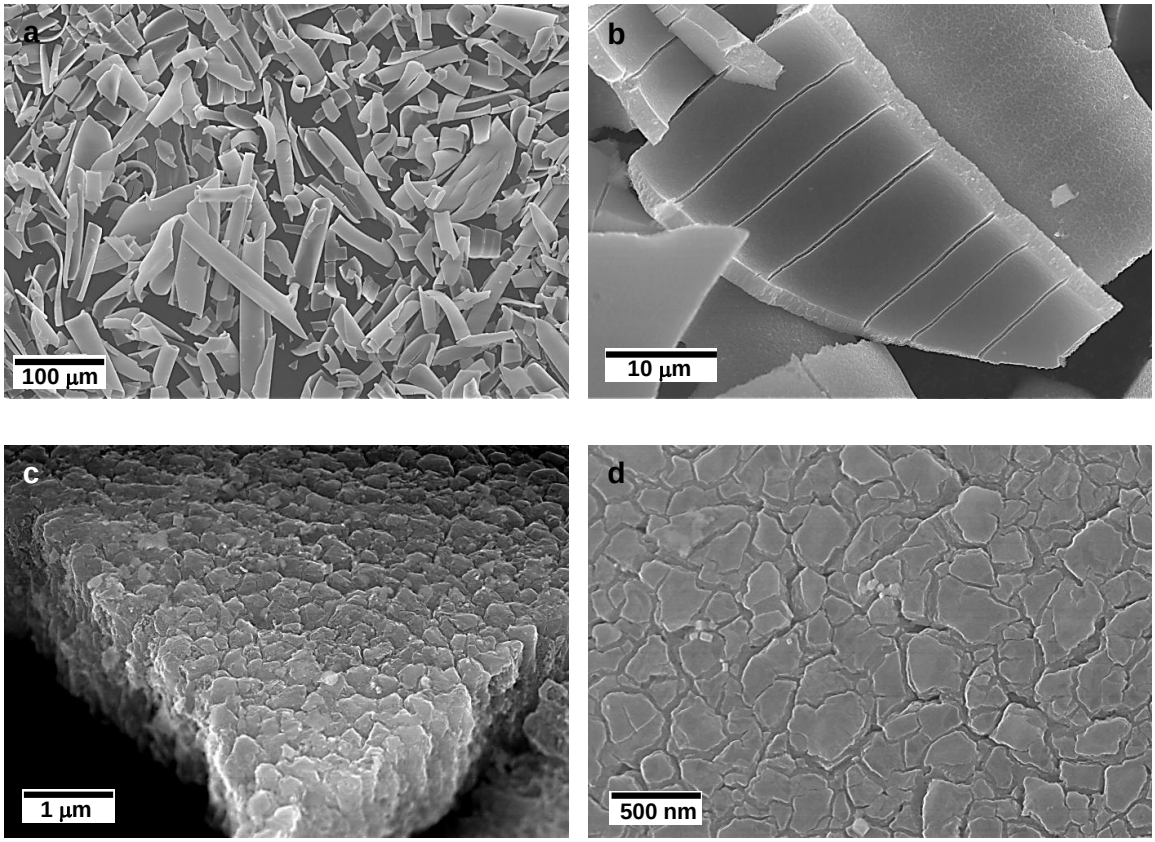


Figure S2. Scanning electron microscopy (SEM) micrographs of 1.5 μm thick $Mg_{0.75}Nb_{0.25}$ alloy film after 10 sorption cycles, shown in order of increasing magnification.