Magnesium-ion batteries (MIBs) have twofold volumetric energy density than that of lithium without the dendritic deposition morphology associated with Li, which makes MIBs attractive options. We investigate the feasibility of using anatase-phase TiO₂ as an electrode material for MIBs. Electrochemical, microscopic, and spectroscopic analyses are performed in order to probe Mg-ion insertion as well as determine the limitation of TiO₂ as a viable electrode material.

© 2016 The Electrochemical Society. [DOI:10.1149/2.1091610jes] All rights reserved.
In order to quantify Mg insertion into anatase TiO₂ structure, the electrodes were examined using EDX mapping. It is found that following discharge of the cell to 0.05 V, a magnesium signal is observed in the EDX mapping (Figure 3a). Quantitation of this result leads to a Mg:Ti ratio of ∼0.1:1, which is also signified from the initial discharge capacity. To determine the ability of Mg to reversibly shuttle between the working electrode and counter electrode, magnesiated TiO₂ electrode was charged to 2.2 V and removed for SEM/EDX analysis. No obvious magnesium signal is seen in the EDX mapping (Figure 3b), indicating that magnesium ions can reversibly diffuse between the magnesium metal counter electrode and titanium dioxide working electrode.

As discussed above, a Mg:Ti ratio of ∼0.1:1 can be inserted into anatase TiO₂ through electrochemical method. Chemical magnesiation was conducted using a method shown in scheme 1 to investigate the limitation of Mg insertion into anatase TiO₂. A vivid color
Figure 3. (a), (b) SEM/EDX mapping for the TiO$_2$ electrode at fully discharged and charged states, respectively.

Figure 4. (a) Chemical magnesiation process and samples obtained; (b) UV–vis spectra for the pristine and magnesiated samples.

Insertion of an electrochemically active ion into a host structure reduces one of the metal ions in the host structure. As a result, the energy difference between the valence and conduction bands of the host metal ion changes upon intercalation. This phenomenon is observed in the lithiation of TiO$_2$.\textsuperscript{11} Therefore, as another method to verify the magnesium insertion into the anatase TiO$_2$ host structure, UV–vis spectra were carried out for the pristine and magnesiated samples (Figure 4b). As summarized in Table II, the interception wavelength of magnesiated sample increases radically compared to that of pristine TiO$_2$, which confirms that magnesium insertion changes the energy difference between the valence and conduction bands of the host structure. The decrease of bandgap leads to improvement of the electronic conductivity of TiO$_2$ after magnesiation, which indicates a good rate capability as shown in Figure S4. The material still exhibits a discharge capacity of $\sim 45$ mAh g$^{-1}$ at a current density of 40 mA g$^{-1}$.

Conclusions

Both spectroscopic and microscopic techniques confirm that a Mg:Ti ratio of $\sim 0.1:1$ can be inserted into anatase TiO$_2$ electrochemically or chemically without phase transformation. The different insertion ability of lithium and magnesium ions into anatase TiO$_2$ once more manifests the sluggish kinetics of Mg$^{2+}$ ion diffusion process.

Acknowledgments

The authors acknowledge the support by the seed funding from Sustainable Power and Energy Center under the Frontier of Innovation Award by Vice Chancellor of Research at UC San Diego. H. L. acknowledges the China Scholarship Council under Award No. 2011631005. All the authors appreciate the assistance of Dr. Yang Ren at beamline 11-ID-C of Argonne National Laboratory.

References