Pseudocapacitive Mg^{2+} Storage Properties of Interlayer-expanded VS_2 Nanosheets by Electrochemical In-situ Doping of PP_{14}^{+}

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Magnesium rechargeable batteries (MRBs) have attracted intensive attention as a promising alternative to Li-ion batteries[1]. Nonetheless, the intense polarization effect of Mg^{2+} and large Mg^{2+} dissolvation energy of traditional chloride-based electrolytes have seriously halted the practical applications of MRBs[2]. Herein we reported a high performance MRB using a VS_2 nanosheets cathode and a 0.4 M $(PhMgCl)_2$-$AlCl_3$/ tetrahydrofuran (APC) electrolyte with 1-butyl-1-methylpiperidinium chloride ($PP_{14}Cl$) as an electrolyte additive. First-principles calculations, spectroscopic techniques and electrochemical experiments showed that 0.43 mol of PP_{14}^{+} was electrochemically doped into 1 mol of VS_2 nanosheets during early stage of the first discharge. As a result, the interlayer spacing of the nanosheets was expanded form 0.57 nm to 1.10 nm. In the meanwhile, the material structure transformed from the 1T phase to the 2H phase. The expanded VS_2 interlayer spacing significantly improved the diffusion kinetics of Mg^{2+}, resulting in large reversible capacity (348 mAh g^{-1} at the 0.1C rate) and excellent rate capability (213.8 mAh g^{-1} at the 10C rate). A maximum specific energy of 243.7 Wh kg^{-1} and maximum specific power of 1513 W kg^{-1} were obtained, which were among the best results of state-of-the-art MRBs. Quantitative kinetic analysis indicated that 91.7% of the specific capacity was attributed to pseudocapacitance owning to the expanded interlayer spacing and surface redox behavior of the VS_2 nanosheets. This work represents a significant step towards developing high performance and practical usable MRBs.

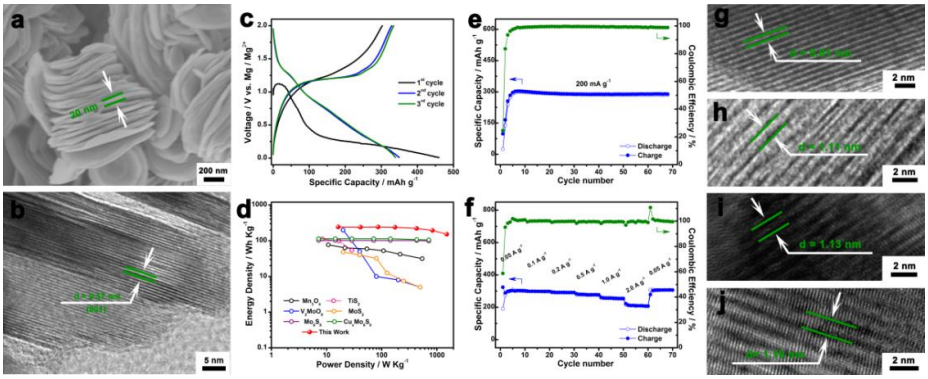

Figure1. (a) SEM, (b) TEM images of VS_2 nanosheets; (c) Charge-discharge profiles of VS_2 in the $PP_{14}Cl$-APC electrolyte at 20 mA g^{-1}; (d) Comparison of energy and power density of this work with state-of-the-art MRBs; Cycle (e) and rate (f) performance; Ex-situ-TEM images of the VS_2 nanosheets; (g-i: 1st discharge to 1.0 V, 0.5 V and 0.01 V; j: 1st charge to 2.0 V).

References:

[1] J. Muldoon, C.B. Bucur, T. Gregory, *Angew. Chem. Int. Ed.* 56 (2017) 12064–12084.
[2] H.D. Yoo, I. Shterenberg, Y. Gofer, G. Gershinsky, N. Pour, D. Aurbach, *Energy Environ. Sci.*, 6 (2013) 2265–2279.