

Investigation of Polyvalent Cation Insertion Reactions Into Transition Metal-Based Host Structures

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High-energy-density, electrochemically rechargeable energy storage systems are the key to the future implementation of a myriad of next-generation applications ranging from biomedical devices to electric vehicles. Currently, there exist two commercialized single-ion room-temperature secondary battery technologies utilizing intercalation electrodes: NiMH (H^+) and Li-ion (Li^+). The basic Li-ion battery utilizes intercalation reactions of Li^+ into transition-metal positive electrodes or carbon-based negative electrodes. Presently, Li-ion technology is the highest energy density commercialized rechargeable battery technology. Although much research has been focused on the improvement of the host electrodes for Li-ion guest cation intercalation, little work has been directed towards the use of alternative guest-cation species to replace the Li^+ cation and studying their resulting physical and electrochemical properties.

The use of Na^+ as a low-cost, potentially less reactive cation for rocking-chair intercalation batteries has been the most prevalent of the reported research on alternative guest-cation intercalation systems¹. Fewer papers have targeted the intercalation reactions of polyvalent cations in order to develop alternative rocking chair cells using guest cations with valences greater than 1. Of these, the development of Mg^{2+} -based batteries and related electrolytes^{2,3,4,5} are the most widely known. Electrochemical intercalation of Mg^{2+} into a number of metal oxides and sulfides has been investigated, especially by Novak et al., however, electrochemical intercalation of these polyvalent cations was accomplished to only a limited degree^{6,7,8,9,10}. The poor utilization of intercalation compounds when polyvalent guest cations are involved can be traced to diffusion limitations. Diffusion of polyvalent cations through inorganic metal oxide or sulfide is slow. This diffusion limitation can be attributed to the large charge density of these cations. During intercalation into a host metal oxide or sulfide structure, these cations will be affected to a greater extent by localized coulombic forces. Le et al.⁸ have recently investigated the intercalation of Mg^{2+} , Al^{3+} , and Zn^{2+} into amorphous aerogel V_2O_5 . Large equivalent capacities comparable with that of Li, were observed. However, all initial intercalation was carried out chemically and no capacity advantage over Li intercalation was noted.

We have recently shown for the first time that polyvalent cation insertion (Fig. 1) into optimized host metal oxide structures can result in improved electrochemical characteristics as compared with Li^+ . This was accomplished with the use of optimized host structures such as nanocrystalline oxides^{11,12}. The redox reaction of the host transition metal determines the maximum achievable specific capacity. We attributed the improved performance to guest ion-host interactions and their resulting influence on host structure transformations. These can also modify, to a large extent, the voltage

profile of the insertion reaction.

The higher reduction potential of polyvalent cations results in a theoretically lower output voltage electrochemical cell compared with Li metal. Nonetheless, we feel that such studies offer valuable insight into understanding of the intrinsic energy density limitations of intercalation compounds and can lead to improved electrode materials for both polyvalent and Li-ion batteries.

In this paper we will report on polyvalent cation insertion into host compounds ranging from nanocrystalline to aerogel materials. Special attention will be focused on the characterization of polyvalent cation diffusion into the host structures and resulting structural impact as determined by X-ray diffraction analysis.

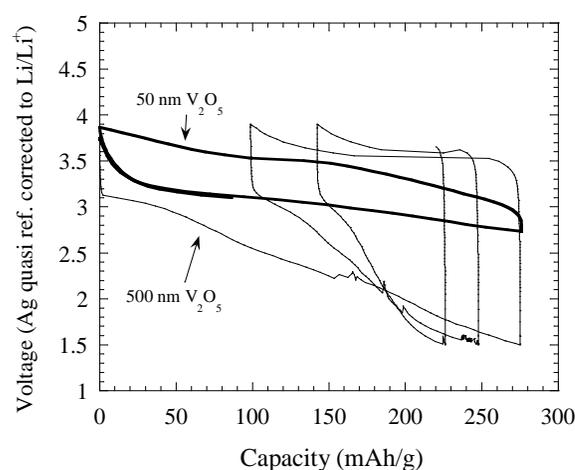


Fig. 1 Discharge / Charge voltage profile of Y^{3+} insertion into macocrystalline and nanocrystalline V_2O_5 host structures

References

1. Y. Ma, M. M. Doeff, S. J. Visco, L. C. De Jonghe, J. Electrochem. Soc., 140, 2726 (1993)
2. C. Liebenow, Electrochimica Acta, 43, 1253 (1998)
3. J. L. Acosta and E. Morales, Electrochimica Acta, 43, 791 (1998)
4. T.D. Gregory, R. J. Hoffman, R. C. Winterton, J. Electrochem. Soc., 137, 2806 (1990)
5. D. Aurbach et al., IMLB 10 Cuomo, Italy June 1, 2000
6. T. Gregory, R. Hoffman, and R. Winterton, J. Electrochem. Soc., 137, 775 (1990)
7. P. Novak, W. Scheifele, F. Joho, and O. Haas, J. Electrochem. Soc. 142, 2544 (1995)
8. P. Novak and J. Desilvestro, J. Electrochem. Soc., 140, 140 (1993)
9. V. Shklover and T. Haibach, J. Solid State Chem., 123, 317 (1996)
10. D. B. Le, S. Passerini, F. Coustier, J. Guo, T. Soderstrom, B. B. Owens, and W. H. Smyrl, Chem. Mater., 10, 682 (1998)
11. G. Amatucci, 102nd Meeting of the American Ceramic Society, St. Louis Mo., May 2, 2000
12. G.G. Amatucci et al., 198th ECS Meeting Phoenix, AZ, Oct. 22-26, 2000, Abstract #215