

# Factors influencing the Electrochemical Behavior of Sulfur-doped Aluminum-substituted Lithium Manganese Oxide Spinel in Lithium Cells

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The synthesis and electrochemical behavior of  $\text{LiAl}_{0.25}\text{Mn}_{1.75}\text{O}_{3.97}\text{S}_{0.03}$ , a novel sulfur-doped spinel, has recently been described.<sup>1,2</sup> In contrast to other manganese oxide spinels, it shows excellent reversibility even when cycled at 3V vs. Li or at elevated temperatures. Because of the large difference in size between oxygen and sulfur anions ( $1.32 \text{ \AA}$  vs.  $1.84 \text{ \AA}^3$ ), it is not likely that sulfur resides in the bulk of this close-packed structure, but rather is present on the surface. This is supported by the unusual idiomorphic particle morphology seen in scanning electron micrographs of samples used for references 1 and 2, which we have also observed.

We believe that the atypical particle morphology is caused by the presence of  $\text{Li}_2\text{S}$  (and other sulfur-containing compounds) during calcination and may be responsible for the robust cycling behavior of these spinels. To test this theory, we synthesized samples from acetate precursors and  $\text{Li}_2\text{S}$  using the sol-gel method described by Park et al, and also by a solid-state method. We also prepared samples by sol-gel and solid-state methods without using  $\text{Li}_2\text{S}$ . Phase-pure spinels with lattice constants of  $8.19 \text{ \AA}$  were obtained, but there were no substantial differences in particle morphologies or sizes among the samples. In all cases, the powders were comprised mainly of very small particles partially fused together to form a porous matrix (Figure 1). Occasionally, smooth particles were seen in the samples processed with  $\text{Li}_2\text{S}$ , but the striking particle morphology seen in the samples made by Park et al. was not observed.



**Figure 1.** Scanning electron micrograph of a  $\text{LiAl}_{0.25}\text{Mn}_{1.75}\text{O}_4$  spinel made by a sol-gel method using  $\text{Li}_2\text{S}$ .

It is difficult to control the air oxidation of  $\text{Li}_2\text{S}$  during the sol-gel process (or during grinding of powders for solid state synthesis) and during calcination of samples. In the absence of sulfur, the particle morphology

is mainly controlled by the release of  $\text{CO}_2$  gas from the acetate precursors. No sulfur was detected by electron dispersion spectroscopy (EDS, detection limit  $\sim 1\%$ ) in the porous portion of samples processed with  $\text{Li}_2\text{S}$ , although some was detected in the smooth particle shown in Figure 1. Additionally, some heterogeneity in the aluminum content of particles was observed in all the samples.

The effect of the particle morphology and electrode composition on the electrochemical characteristics of these materials will be discussed at this presentation.

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## References

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