

PEO-Li_{1.3}Ti_{1.7}Al_{0.3}(PO₄)₃ Composite for Solid Electrolytes in Batteries

K.A. Perry,* W.E. Tenhaeff,* and K.S. Reeves*

*Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN

Rechargeable Li and Li-ion batteries are being developed for portable electronics, electric vehicles, and energy storage for renewable solar and wind. However, rechargeable batteries degrade with charge-discharge cycling and continue to experience significant safety issues. The degradation in performance and flammability concerns can be attributed to the liquid state of the electrolyte. Li metal and Li-ion batteries with solid electrolytes have several advantages, including a higher specific energy density of lithium metal versus graphite, enhanced safety due to reduced flammability, and the potential to minimize failure caused by the formation of lithium dendrites and cracks. It has been proposed that the solid electrolyte must have a shear modulus higher than Li metal [1] and a toughness to accommodate the volume changes and roughening of Li-metal during cycling [2]. It is a challenge to balance the Li conductivity and mechanical integrity in a single electrolyte material; therefore, composites that combine the strength of ceramics with the toughness of polymers are being investigated as solid electrolytes for rechargeable batteries. Microstructural characterization of these composite materials was performed to identify the possible phases that may form at the interface of the ceramic particles and the polymer matrix. Additionally, electrochemical characterization has been used to monitor changes in conductivity and interfacial resistance.

A composite of polyethylene oxide (PEO) doped with LiN(SO₂CF₃)₂ salt and particles of Li_{1.3}Ti_{1.7}Al_{0.3}(PO₄)₃ was the focus of this study. A freeze-fractured cross-section was imaged in a high-resolution scanning electron microscope (SEM). The material was composed of a relatively homogeneous dispersion of particles within a polymer matrix (Fig. 1). The particles ranged in size from <0.5 μm to several micrometers and were enriched in Al and P; conversely, the smooth polymer matrix was enriched in F. This indicated that the LiN(SO₂CF₃)₂ salt was retained in the PEO phase.

To characterize the particle/polymer interface, cryo-transmission/scanning transmission electron microscopy (TEM/STEM) was performed on thin cryo-microtomed sections of the composite, which were cryo-transfer to a Hitachi HF3300 TEM/STEM. A high-angle annular dark-field (HA-ADF) image of the composite is shown in Fig. 2. The bright particles are enriched in the higher Z elements dispersed in a low Z (PEO phase) matrix. Individual Li_{1.3}Ti_{1.7}Al_{0.3}(PO₄)₃ particles ranged from nm- to μm-scale and were agglomerated in the composite membrane. Energy dispersive spectrometry (EDS) spot analysis confirmed the enrichment of Ti, O, and P in the particles (Fig. 3). The atomic ratio of P:Ti = 2 agreed with the expected ratio of 3:1.7 ≈ 2. Additionally, the Al found in the particles was a tenth of the P atomic percentage. The polymer phase was slightly enriched in F and S, which further supported the presence of the LiN(SO₂CF₃)₂ salt in the PEO phase. The interface of a Li_{1.3}Ti_{1.7}Al_{0.3}(PO₄)₃ particle and the polymer matrix is shown in Fig. 4. No obvious reaction zone was observed at the surface of the particles, which is a critical observation since the formation of a separate phase at the surface of the particles could limit Li ion conductivity and/or lead to nucleation sites for mechanical failure that could permit detrimental dendrite

formation and crack propagation. The microstructural characterization will be correlated with conductivity testing of the composite material. Initial results indicate optimization of particle loading and processing is required [3].

References

- [1] Monroe and Newman, *J. Electrochem. Soc.* **152** (2005) A396.
- [2] Orsini et al., *J. Power Sources.* **76** (1998) 19.
- [3] Research sponsored by: ORNL's Laboratory Directed Research and Development Program; ORNL's SHaRE User Facility, sponsored by the Office of Basic Energy Sciences; and the ORNL Weinberg Fellowship (WT), managed by UT-Battelle, LLC, for the U. S. Department of Energy.

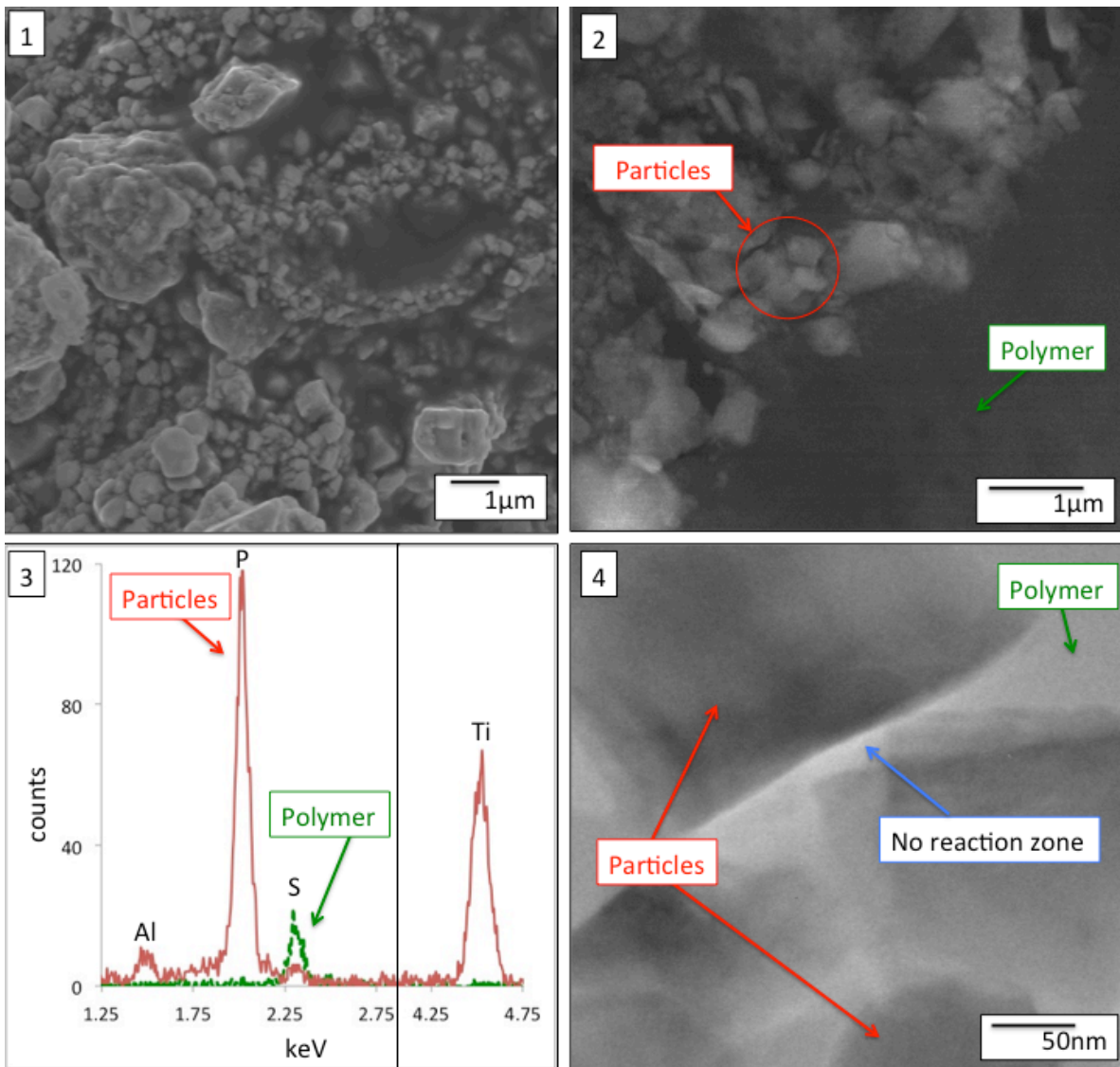


FIG. 1. SEM image of a freeze-fractured cross-section of composite electrolyte composed of PEO with $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ salt and $\text{Li}_{1.3}\text{Ti}_{1.7}\text{Al}_{0.3}(\text{PO}_4)_3$ particles.

FIG. 2. HAADF-(cryo)-STEM of PEO- $\text{Li}_{1.3}\text{Ti}_{1.7}\text{Al}_{0.3}(\text{PO}_4)_3$ composite.

FIG. 3. EDS analysis of individual phases corresponded to expected compositions.

FIG. 4. Bright field TEM image of composite - no obvious reaction zone at the surface of the ceramic particles was observed.