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UC-900

Final Report

CRADA with Chemetals and Pacific Northwest National Laboratory (PNL-051):

Development of Mixed Oxides for Electronic Device Applications

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Final Report
for
ER-LTA CRADA PNL-28

DEVELOPMENT OF MIXED OXIDES FOR ELECTRONIC DEVICE APPLICATIONS

Pacific Northwest National Laboratory
And Chemetals

Purpose/Objective

The purpose of this project is to develop lithiated metal oxides by the glycine-nitrate process for use in secondary batteries. Lithiated manganese oxides are expected to be used in future production of lithium ion systems, now commercially available with a cobalt cathode, and the lithium polymer system, which is becoming commercially available with a vanadium oxide cathode. The lithiated manganese cathodes are expected to have price advantages, due to lower cost, larger supply, and lower toxicity of manganese as compared to cobalt and vanadium. The lithium polymer system is expected to be used as a power source for electric vehicles later in this decade.

The glycine-nitrate process is a combustion synthesis technique that is particularly well-suited to producing high-quality, active, mixed inorganic oxides at relatively low cost. The glycine-nitrate process was developed and patented on previous DOE sponsored projects.

Summary of Activities Performed

Approximately one hundred batches of lithiated manganese oxides were prepared in the laboratory using the glycine-nitrate method. The had various lithium-to-manganese ratios and were produced under various combustion stoichiometries (glycine-to-nitrate ratios). Raw synthesized samples were subjected to a variety of calcinations in air, including various two-stage heat treatments. Characterization of the combustion synthesized samples included surface area via nitrogen adsorption, x-ray diffraction, and wet chemical titration to determine oxidation state.

Larger batches of lithiated manganese oxides were prepared in the continuous glycine-nitrate reactor that had been developed and constructed on an earlier ER-LTA CRADA project. Each of these batches was several kilograms. These production scale runs were produced at a range of combustion stoichiometries.

The objective of the synthesis procedure development was to find the combination of combustion stoichiometry and subsequent heat treatment conditions that maximized the fraction of spinel phase ($LiMn_2O_4$), maximized the powder tap density, and minimized the powder surface area, while maintaining acceptable electrical characteristics. Minimal post-synthesis heat treatments were preferred in order to decrease manufacturing costs. Electrical characteristics were determined at Chemetals by building "button cell" batteries that used the lithiated manganese spinel as the cathode in combination with other standardized battery components. Performance of the PNNL-supplied samples was compared to that of samples produced by a proprietary synthesis technique developed at Chemetals. Samples were compared on the basis of initial battery capacity (mah/g), percent fade at 10 cycles, and percent capacity at 100 cycles. Propriety criteria were supplied by the partner.

Significant Accomplishments

A range of fuel-lean combustion conditions was found that produced >99% of the desired spinel phase after a one hour post-synthesis heat treatment at moderate temperatures. These conditions were replicated in the continuous production reactor, and at least one sample was produced in the reactor that had excellent electrical properties in battery tests at Chemetals.

Significant Problems

The project ended with Chemetals deciding to drop development of the glycine-nitrate process in favor of their proprietary in-house process for synthesis of the lithiated manganese spinel. Apparently, they were able to produce powders that had comparable, or at least acceptable electrical properties but that had higher tap densities. The requirement for high tap density was not explained to PNNL investigators until late in the project, so only a few months was available to attempt to achieve this requirement. Another problem was that the long time necessary to complete testing of the electrical properties of samples supplied by PNNL resulted in a slow developmental feedback loop.

DOE/Laboratory Benefits Realized

The glycine-nitrate continuous reactor capability benefitted by experience in producing several kilograms of the lithiated manganite spinel. Understanding of the relationships between combustion stoichiometry and phases produced will be beneficial for the later production of similar multi-phase materials containing multivalent cations.

Industry Benefits Realized

The industrial partner was able to assess the potential technical and economic benefits of combustion synthesis as compared to their proprietary synthesis technique.

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