Mixed Polyanion Glasses as Lithium Ion Battery Cathode Materials

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Lithium iron phosphate is a commercially successful crystalline polyanionic material for use in lithium ion battery cathodes that has excellent specific capacity, cycleability, and safety performance. The success of lithium iron phosphate has lead researchers to explore other crystalline polyanionic materials [1-3], such as $LiCoPO_4$, $LiCoBO_3$, and Li_2MnSiO_4, which have higher theoretical capacities and/or higher redox potentials. Unfortunately, the experimentally measured capacities of these other crystalline polyanionic materials have not approached their excellent theoretical values typically due to low electrical conductivity and/or irreversible phase changes during cycling.

In this paper, mixed polyanion glasses have been demonstrated as a new class of cathode materials that could actually achieve the excellent theoretical capacities of similar crystalline polyanionic materials by having higher electrical conductivity and no crystal structure changes. Electrical conductivity enhancement of glasses by orders of magnitude can be achieved by partial substitution of polyanions, such as vanadate or molybdate, for the network former in the glass (phosphate, borate, or silicate) [4]. Polyanion glasses do not undergo crystalline phase changes as lithium anions cycle in and out of their structure.

Mixed polyanion glasses can be made by conventional melt-quench processing. Iron phosphate vanadate glasses have been made from the melt by graphite glass casting and splat quenching (FIG. 1). Special attention must be placed on the stable transition metal valence state under processing conditions.

Proof-of-principle of the mixed polyanion glass concept has been demonstrated. Iron pyrophosphate glasses have shown dramatic improvements in electrochemical performance with increased vanadate substitution (FIG. 2). The specific capacity of iron pyrophosphate glass was negligible, but iron pyrophosphate glass with 50% vanadate substitution demonstrated 100% theoretical capacity. In comparison, Padhi, et al. [5] have produced crystalline iron pyrophosphate cathodes that have only achieved 75% theoretical capacity. Future research efforts have shifted to pursuing mixed polyanion glasses with high specific energies.

FIG. 1. Splat quenching an iron phosphate glass melt (glass melt in glowing hot crucible about to be poured onto bottom copper chill plate)

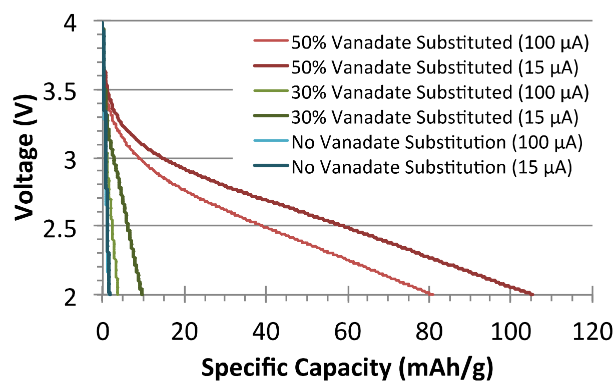

FIG. 2. Discharge curves of iron pyrophosphate glasses with different amounts of vanadate substitution (100 µA and 15 µA correspond to ~C/5 and ~C/30)

Acknowledgments:

Financial support for this project came through the Batteries for Advanced Transportation Technologies program as managed by the U.S. Department of Energy Vehicle Technologies Office. The authors acknowledge the technical assistance of Roberta Peascoe-Meisner, Paul Menchhofer, Jagjit Nanda, Surrendra Martha, Hui Zhou, Loic Baggetto, and Gabriel Veith of Oak Ridge National Laboratory and Frank Delnick of Sandia National Laboratory.

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