ALL-SOLID-STATE RECHARGEABLE LITHIUM ION BATTERY FABRICATION WITH Al-DOPED $Li_7La_3Zr_2O_{12}$ SOLID ELECTROLYTE

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INTRODUCTION

Compared with liquid organic electrolytes, lithium ion conductive solid electrolytes offer improved safety, reliability and leakage-free properties, as well as the advantages wider electrochemical voltage ranges, better chemical compatibility, and the possibility for structural batteries. Among all the solid electrolyte materials, garnet-$Li_7La_3Zr_2O_{12}$ (LLZO), with relatively high ionic conductivity (~ 2 x 10^{-4} S cm^{-1}, RT), has attracted much attention since first being reported (1).

To achieve high conductivity, prolonged sintering time at 1200 °C was necessary with conventional solid state synthesis method. Al doping was reported to reduce the synthesis time and stabilize the highly conductive cubic LLZO phase (2). In this work, Al-doped LLZO was synthesized by the Pechini method and a solid state battery was fabricated by a low temperature process. A 0.5 mm thick Al-LLZO slice was applied as the electrolyte. $Cu_{0.1}V_2O_5$ - carbon composite slurry and Li metal were used as the cathode and anode. The composite $Cu_{0.1}V_2O_5$/LLZO/Li battery was successfully cycled at different temperatures. High capacity and good cycle life was achieved at 50 °C.

EXPERIMENTAL

Cu and V_2O_5 powders were dissolved in H_2O_2 solution, dried at 130 °C, and the residue was calcined at 300 °C for 5 hours to form $Cu_{0.1}V_2O_5$ powder. The powder was ball mixed overnight with carbon black and binder (a combination of styrene-butadiene-rubber and sodium-carboxyl-methyl-cellulose in a 1:1 wt. ratio) in DI water. The ratio between $Cu_{0.1}V_2O_5$, carbon black, and binder was 80:15:5 (wt %).

Details about the Pechini synthesis of the Al-doped LLZO pellet can be found in (2). The Al-LLZO pellet was sliced and progressively polished through 1 µm grit diamond until it was approximately 0.5 mm thick. About 0.4 mg cathode slurry was pipetted onto the LLZO and dried at 120°C. The area of the cathode was about 0.5 cm^2. In an Ar filled glovebox, Li foil was melted at 200°C and attached to the other side. Copper foil was attached to the molten Li as the anode current collector. The Li side was capped with a thermal wax to protect it from the ambient upon removal from the glovebox. Colloidal Ag paint was applied to the cathode side as the current collector. Battery cycle results were collected by an Arbin battery tester.

RESULTS

At 50 °C, the battery had 176 mAh g^{-1} capacity (calculated based on the cathode material weight) for the first discharge when cycled with 5 µA cm^{-2} current density. Almost 100% coulombic efficiency was achieved for the first cycle. When tested at a 10 µA cm^{-2} current density, the initial discharge capacity decreased to 93 mAh g^{-1}. After 20 cycles, the capacity decayed to 68.6 mAh g^{-1} (73.8% of the initial value).

The successful cycling results indicate that the Al-dope LLZO is a promising solid electrolyte material. Also, the low temperature slurry coating method was proved as a simple and convenient way to fabricate solid state batteries.

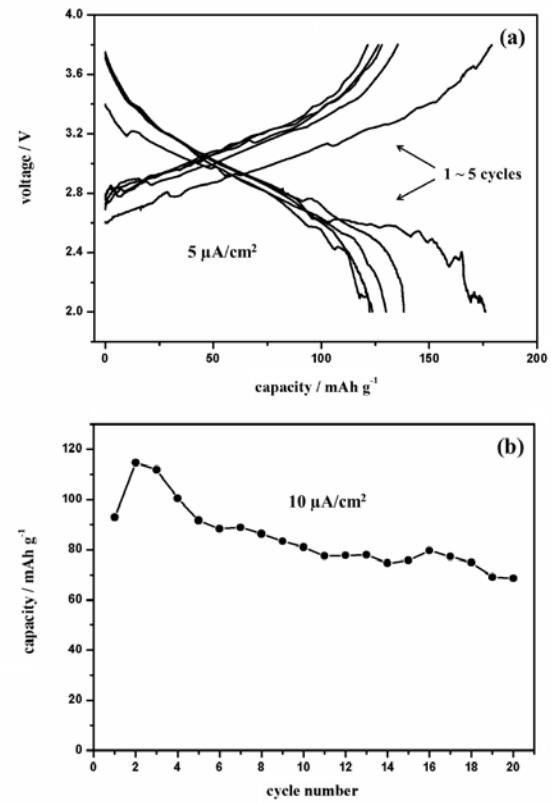

Figure 1: (a) Charging and discharging curves of the $Cu_{0.1}V_2O_5$/LLZO/Li battery tested at 50 °C. current density: 5µA cm^{-2}. Cut off voltage range: 2.0V~3.8V. (b) battery capacities of the first 20 cycles when tested at a 10 µA cm^{-2} current density at 50 °C..

REFERENCES

1. R. Murugan, V. Thangadurai, W. Weppner. Angew. Chem. Int. Ed. 46 (2007) 7778.
2. Y. Jin, P.J. McGinn. J. Power Sources 196 (2011) 8683.