

Improved Rate Properties of Li-ion Battery Consisting of ZrO₂ Modified Graphite Anode and Substituted Spinel Cathode

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Introduction

Li-ion batteries are superior in terms of specific energy and power and also have the potential to be “the battery of choice” for Hybrid Electric Vehicles (HEVs). However, the low rate capability, high cost, and the safety performances limit its successful application. The main factor affecting the poor performances seem to be the carbon anode and have been investigated extensively [1]. Recently we reported improved rate properties by surface modification of natural graphite with ZrO₂ considering a half cell (C/Li) [2]. However, a full cell study of the improved anode and cathode is important for practical application. Here we present the performances of ZrO₂ modified graphite anode in Li-ion full cell using LiMn_{1.8}Co_{0.2}O₄ as the cathode. A Li-ion cell consisting of above anode and cathode gives exceptional rate capability long life, cheaper and abundant material usage, and cover majority of necessary requirements for HEVs.

Experimental

ZrO₂ modified graphite was prepared as described previously [2]. LiMn_{1.8}Co_{0.2}O₄ was prepared by a solid state method using a stoichiometric mixture of Li₂CO₃, Co (CO₂)₂·2H₂O and Mn₂O₃ and the electrode was prepared on Al-foil as reported [3]. First cycle of graphite electrode was charge-discharged at 0.2C rate between 2.5-0.01V using Li-metal as the counter electrode before assembling into the full cell. The electrodes were assembled into beaker type two electrode cell using LiMn_{1.8}Co_{0.2}O₄ as the working electrode, pre-cycled graphite as the counter electrode and 1M LiClO₄ in EC/DEC as the electrolyte and was galvanostatically cycled between 4.2-3.2 V vs Li/Li⁺. For comparison, a cell comprising of untreated graphite as the anode was also studied.

Results and discussion

In the present study we concentrated on several factors in constructing the full cell. (1) The cathode/ anode mass in the cell was optimized (cathode: anode wt. =3:1). (2) The first cycle of graphite electrode was charge-discharged at fairly slower C rate (0.2C rate) reference to the Li-metal for the stable film formation on the surface of graphite (This is a novel approach taken to improve the cycle stability and rate properties and further investigation is in progress). (3) The Charge-discharge voltage range is 4.2-3.2 V.

The presence of monoclinic ZrO₂ on the surface graphite was detected by XRD and X-ray absorption near edge structure analysis. Fig. 1 shows the voltage profile of the full cell consisting of Zr-treated (C_{Zr}) and untreated graphite (C) anode and LiMn_{1.8}Co_{0.2}O₄ cathode at 1st, 2nd, and 15th charge-discharge cycles at 1C rate. Both cells show an average voltage of 3.8 V during the discharge. Discharge capacity upon cycling of each cell was shown in Fig. 2. At 1C rate, both cells deliver similar cycle performance that LiMn_{1.8}Co_{0.2}O₄ half cell showed at the same rate. This indicates that the efficiency of the cell is almost similar to LiMn_{1.8}Co_{0.2}O₄ half cell [3]. Although, the untreated cell was capable to deliver comparable capacity and its retention at 1C and 2C rates, it showed poor performances at higher rates. It is interesting to note that Zr-treated cell was capable to deliver 80% of its initial discharge capacity even at 5C rate. When charge-discharge current was reduced back to 1C rate after higher rate cycling, Zr-treated cell shows steady performance where as untreated cell continues to decay. It is believed that the presence of ZrO₂ crystallites on the surface assists typically

formed surface protective film to better protect graphite from destruction upon cycling and the improved charge transfer kinetics leads to a high rate charge-discharge capability. The capacity fading observed in the untreated cell is presumably resulted from gradual destruction of graphite on cycling. The details of the surface modification and its affect on the cycle and rate capabilities are still under investigation.

Acknowledgement

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References

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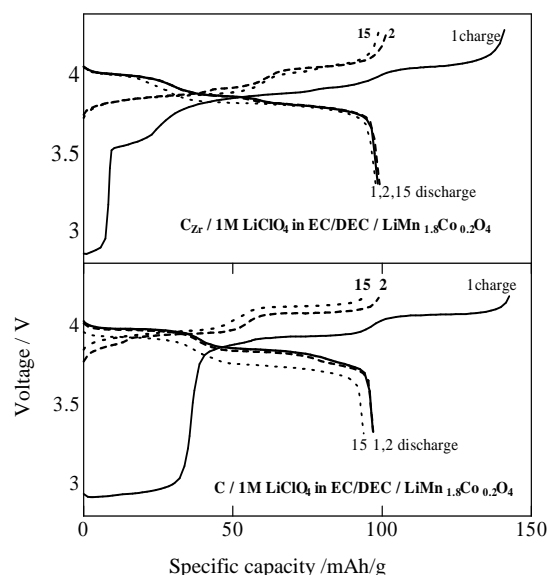


Fig. 1 Voltage profile of the full cell.

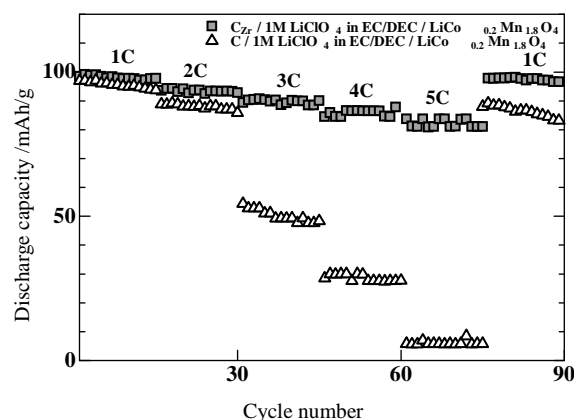


Fig. 2 Cycle performance of the full cell.