High rate performance of manganese oxide nano-coated on acetylene black by sonochemical method

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Sonochemical synthesis has been recently attracted much attention because of its advantage for processing nanomaterials. In this work, nano-layer amorphous manganese oxides coated on carbon powders are synthesized through sonochemical treatment of permanganate. The thickness of amorphous manganese oxide formed on a carbon particle was uniform and about several nanometers. The condition and dimension of the coating materials is controlled by pH of solutions and sonication period. The high rate discharge properties as electrode of lithium battery were investigated and found to exhibit both high energy density and high power density. Such good performance might be ascribed to rapid electrochemical reaction on the high surface area of the coating structures and short diffusion distance of lithium in thinly coated material.

Manganese oxide nanoparticles were often synthesized by reduction of MnO_4^- with reduction agents in a solution. In this work, MnO_4^- anion was reduced by reductant species that was induced by sonication on the solution. 750 ml of sodium permanganate solutions with a concentration of 0.01 mol/l were prepared (pH=10). 0.65 g of acetylene black was added. These solutions were stirred and sonicated with frequency of 100 kHz and power of 600 W for 1 ~ 6 hours. In order to examine the influence of pH of solution in addition to above, permanganate solution whose pH was lowered below unity by a portion of perchlorate acid was also tested. Composite powders obtained were filtrated, washed several times with deionized water and dried at 120°C for 12 hours in air. The structure of samples was investigated by Xray diffraction. Morphologies of the composite powders were observed by TEM. Charge-discharge were tested between 4.3 ~ 1.5 V versus Li^+/Li with current densities of 0.01 ~ 10 A/g. The unit of current density was based on the weight of used composite powder including acetylene black. Three electrode cell was assembled in Ar atmosphere. The specimen for working electrode was formed by mixing the composite powder with 5 wt% of Teflon and spreading on Ni mesh as a current collector. Lithium metal was used as both counter and reference electrode. 1mol/l $LiClO_4$/(EC+DMC) was used as a electrolyte solution.

Yields indicated that the reduction in pH<1 solution was much faster than that in pH=10 solution. The XRD profiles revealed that not only amorphous manganese oxide but also birnessite phase exists in these powders.

Figure 1 shows TEM micrograph of amorphous manganese oxide nano-coated on surface of acetylene black synthesized by 6-hours sonication in pH=10 solution. In this specimen, most of manganese oxide was formed as not particle but layer 1 ~ 10 nm thick on acetylene black. In general sonochemical reduction, cavitation forms reductants from H_2O, which has only short life time or alcohol if added. In our experiment, no alcohol was used. It is found that reduction of MnO_4^- was not achieved without acetylene black. This fact indicates that acetylene black reduced MnO_4^-. This is probably because the surfaces of acetylene black itself or some kinds of impurities on them generate radical species by sonication. As a result of reduction of MnO_4^- at the surface of acetylene black, amorphous manganese oxide covered uniformly as observed in fig.1.

Figure 2 shows discharge-charge curves of the samples obtained by 1-hour sonication in solution of pH<1. The specific capacity using current density of 0.01 A/g was 70mA/g (based on composite weight), corresponding to 250 mAh/g (based on the weight of active material). In the case of 10A/g, which is 1000 times larger than above, only a slight decline in capacity was observed compared to using 0.01 A/g. This is probably ascribed to the large effective volume of manganese oxide for discharge. That is realized by short distance of lithium diffusion and increase in electrical conductance by uniform and thin coat of manganese oxide.

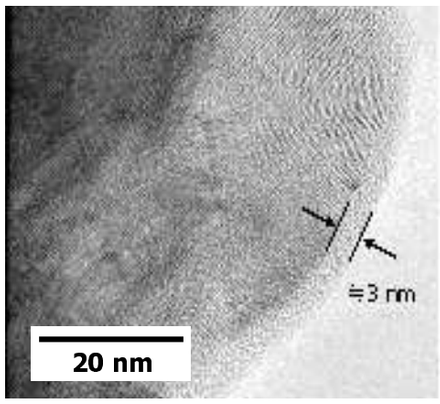

Fig. 1 TEM photograph of amorphous manganese oxide layer on acetylene black.

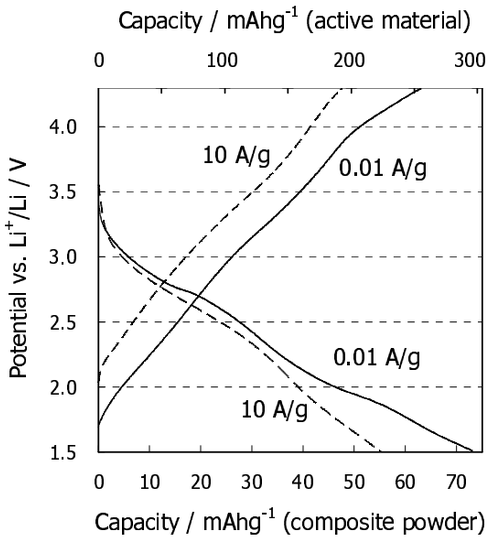

Fig. 2 First discharge and charge curves of MnO_2/AB composite powder synthesized by sonication for 1 hour in pH<1 solution.