論文 / 著書情報
Article / Book Information

題目(和文)	リチウム硫黄電池用新規カソード材料の開発
Title(English)	Development of Novel Cathode Materials for Lithium Sulfur Batteries
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出典(和文)	学位:博士（工学）, 学位授与機関:東京工業大学, 報告番号:甲第10309号, 授与年月日:2016年9月20日, 学位の種別:課程博士, 審査員:谷口 泉,伊東 章,久保内 昌敏,吉川 史郎,森 伸介
Citation(English)	Degree:, Conferring organization: Tokyo Institute of Technology, Report number:甲第10309号, Conferred date:2016/9/20, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	要約
Type(English)	Outline

Thesis outline

This thesis systematically investigates S/C/V_2O_5 composite by diverse strategies. The main results and specific work were conducted as following:

Chapter 1 introduces a general background of Li-ion batteries, including the urgent demand of renewable energy sources and energy conversion, the features of Li-ion batteries and the working principles of Li-ion batteries. Especially, a brief view of existing popular cathode and anode materials are presented according to their electrochemical reaction mechanisms. Based on this view, Li-S battery is induced in consideration of high energy density, low cost and environmental benignity. After that, the recent achievements of Li-S battery are provided, including S/C composite, S/polymer composite, modified electrolyte and S/metal oxide composite. The present problems to overcome in the Li-S batteries were highlighted through this review, and then the objective of this study is presented.

Chapter 2 reports the S/C/V_2O_5 composite prepared by a wet-ball-milling method and its physical and electrochemical properties are studied. Firstly, the effect of the carbon content of S/C composite on their physical and electrochemical properties was investigated. It was found that increasing the carbon content of the S/C composite electrodes led to a higher discharge capacity in each cycle owing to their high electronic conductivity provided by carbon. On the other hand, the S/C composite electrode with 40 wt.% carbon had the best capacity retention after 10 cycles. However, its discharge capacity markedly decreased from 1077 to 606 mAh g^{-1} in 10 cycles, which corresponds to a capacity fading rate of 47 mAh g^{-1} per cycle. To improve the electrochemical performance of the S/C composite electrode,

the partial replacement of carbon by V_2O_5 was performed in the S/C composite. When evaluated as Li|1M LiTFSI in DOL:DME=1:1|S/C/V_2O_5 cells in the potential range from 1.5 to 4 V *vs*. Li^+/Li, the S/C/V_2O_5 composite electrode with 30 wt.% V_2O_5 exhibited the discharge capacities of 718 mAh g^{-1} after 10 cycles and 473 mAh g^{-1} after 50 cycles, which were larger than those of the S/C composite electrode with 40 wt.% carbon. The capacity fading rate of the S/C/V_2O_5 composite electrode with 30 wt.% V_2O_5 was 23 mAh g^{-1} per cycle in the first 10 cycles. In addition, cyclic voltammetry measurements revealed that V_2O_5 component in S/C/V_2O_5 composite was electrochemically active and positively contributes capacity for S/C/V_2O_5 electrode during cycling. As a result, the S/C/V_2O_5 composite electrodes showed better cycling performance than that of S/C composite electrodes.

Chapter 3 introduces a new technique to prepare PN-V_2O_5, namely spray pyrolysis with NH_4NO_3 additive in precursor solution, and the correlation between porous structure and electrochemical properties of V_2O_5 has been investigated for the first time. The primary particles in the PN-V_2O_5 particles became smaller upon increasing the concentration of NH_4NO_3 from 0 to 0.272 mol L^{-1}, and then both mesopores and macropores formed in the V_2O_5 particles owing to the thermal decomposition of NH_4NO_3 in the SP process. Further increasing the concentration of NH_4NO_3 from 0.272 to 0.408 mol L^{-1} promoted only the formation of macropores in the V_2O_5 particles. The change in the porous structure due to the NH_4NO_3 additive in the precursor solution was confirmed by pore structure analysis based on N_2 adsorption-desorption isotherm measurements, which reveal that nanostructured V_2O_5 particles with a pore size of less than 100 nm can be prepared by the novel SP method and that an increase in the NH_4NO_3 concentration in the precursor solution can enlarge the pores

in the V_2O_5 particles, especially those with a size between 20 and 80 nm. The PN-V_2O_5 particles were used as cathode materials for lithium batteries, and their electrochemical performance was investigated using Li|1 M LiTFSI in DMC: DOL = 1:1|V_2O_5 cells at room temperature. The Meso+Macro-V_2O_5 electrode, synthesized at 500 ºC by SP with 0.272 mol L^{-1} NH_4NO_3, exhibited a higher discharge capacity at different charge-discharge rates ranging from 100 to 1200 mA g^{-1} than the Meso-V_2O_5 electrode, synthesized at 500 ºC by SP without NH_4NO_3, and the Dense-V_2O_5 electrode, synthesized at 700 ºC by SP without NH_4NO_3. The superior specific capacity and high rate capability could be attributed to its porous and integrated nanostructure, which provides a large specific surface area, a reduced lithium ion diffusion distance and easy penetration of the liquid electrolyte into the electrode.

Chapter 4 reports the S/C/PN-V_2O_5 composites synthesized by a combination of WBM and heat treatment, and then the effect of heat-treatment parameters (e.g. heating temperature and heating time) and pore structure of V_2O_5 on physical and electrochemical performance of S/C/V_2O_5 composites were investigated. The XRD patterns and FT-IR patterns reveal that higher heat treatment temperature of 200 ºC or long heat treatment time (10 h) can promote the chemical reactions between S and V_2O_5, and this phenomenon was also confirmed by charge/discharge profiles of the samples. The electrochemical performance indicated that the optimum heat treatment parameters (160 ºC for 2h) for the S/C/PN-V_2O_5 composite electrode exhibited a discharge capacity of 666 mAh g^{-1} after 50 cycles, which was higher than that of S/C/PN-V_2O_5 composite electrode without heat treatment (474 mAh g^{-1}). It was also found that the PN-V_2O_5 is more effective to improve the cycling performance of S cathode than that of dense V_2O_5, which might be ascribed to the large surface area of PN-V_2O_5 and better

penetration of S during heat treatment process. Finally, the advantages of PN-V_2O_5 additive for S cathode were highlighted by comparison of the S/C/PN-V_2O_5 and the S/C composites considering discharge capacity and capacity retention. The S/C/PN-V_2O_5 composite electrode displayed a discharge capacity of 666 mAh g^{-1} after 50 cycles and capacity fading rate of 20 mAh g^{-1} per cycle in the initial 10 cycles and 8 mAh g^{-1} per cycle after 50 cycles. On the other hand, the initial discharge capacity of S/C composite electrode was 1114 mAh g^{-1} and decreased to 671 mAh g^{-1} after 10 cycles and remained 379 mAh g^{-1}, corresponding to a capacity fading rate of 44 mAh g^{-1} per cycle during initial 10 cycles and 15 mAh g^{-1} per cycle after 50 cycles.

Chapter 5 presents main conclusions from this study.