論文 / 著書情報
Article / Book Information

題目(和文)	
Title(English)	Development of porous carbon electrode for Li-air battery fabricated from supercritical carbon dioxide technique
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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11479号, 授与年月日:2020年3月26日, 学位の種別:課程博士, 審査員:下山 裕介,伊原 学,久保内 昌敏,多湖 輝興,森 伸介
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number:甲第11479号, Conferred date:2020/3/26, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	応用化学 系 応用化学 コース	
学生氏名： Student's Name	クナーヌソン ナッタナイ	
申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of	(Engineering)
指導教員（主）： Academic Supervisor(main)	下山裕介	
指導教員（副）： Academic Supervisor(sub)		

要旨（英文800語程度）
Thesis Summary (approx.800 English Words)

This work was dedicated to the development of Li-air battery cathode which fabricated by supercritical carbon dioxide drying. In first chapter, the researches on development of Li-air battery including effect of reaction gas, cathode compartment, electrolyte, anode compartment were reviewed. Supercritical carbon dioxide (sc-CO_2) and its application for drying were also introduced in this chapter.

Chapter 2 provides detail of view cell experiment of pure organic solvent in supercritical carbon dioxide at various pressure. It was found that homogeneous phase formation time is shorter in higher pressure condition due to larger amount of sc-CO_2. 1-methyl-2-pyrrolidinone (NMP) in which carbon black (CB) and Polyvinylidene fluoride (PVDF) dispersed was investigated by high pressure view cell to confirm the supercritical carbon dioxide drying process of cathode materials.

In chapter 3, cathodes of Li-air battery were prepared by drying NMP slurry in which carbon black and PVDF binder were dispersed. Supercritical carbon dioxide drying at 10.0 to 20.0 MPa, 40℃ and evaporation at 80℃ were applied as drying methods. The morphology and properties of cathode were investigated by SEM, porosity measurement, conductivity measurement and thermogravimetric analysis. Cathode dried by sc-CO_2 drying at 20.0 MPa, 40℃ was self-standing with thickness around 900 μm and 94% porosity. On the other hands, cathode dried by evaporation was cracked and with 145 μm thickness and 58% porosity. SEM images of cathodes revealed that carbon particle on surface dried by evaporation was aggregated due to high interfacial tension during drying, while porous structure of carbon particle was confirmed on surface dried by sc-CO_2 drying. Furthermore, porosity of cathode increases while sheet conductivity decreases as supercritical drying pressure increases. It is considered that sc-CO_2 dissolves into solvent, causing expansion at higher rate at higher supercritical drying pressure. Therefore, higher porosity structure can be fabricated after solvent elimination at higher supercritical drying pressure. Practical Li-air batteries using ionic liquid as electrolyte and ambient air as reaction gas were tested by varying polymer binder content and supercritical drying pressure in cathode fabrication. 30 times higher specific capacity was achieved after dried cathode with supercritical carbon dioxide instead of evaporation. Cathode fabricated from supercritical drying at 20 MPa, 40℃ provided highest specific capacity at 8.4 mAh cm^{-2} due to its high porosity which can store Li-oxygen product and enhance oxygen diffusivity. It was also found that content of polymer binder in electrode also held the key to improve mechanical strength of electrode

In chapter 4, cathodes with ionogel binder were proposed to enhance discharge performance of Li-O_2/CO_2 battery. Cathode with normal binder was prepared by sc-CO_2 drying of CB/PVDF/MnO_2 in NMP slurry at 20 MPa, 40℃, while cathode with ionogel binder was prepared by sc-CO_2 drying of CB/PVDF/MnO_2/ionic liquid in NMP slurry at 20 MPa, 40℃. 3 types of ionic liquid (IL) were employed which were [bmim][Tf_2N], [bmim][PF_6] and [BMIM][I]. Thermogravimetric analysis of revealed that cathode with ionogel binder has lower decomposition temperature of polymer than cathode with normal binder. This means that ionic liquid was impregnated in polymer binder, forming complex of polymer and entrapped ionic liquid. This complex was called as ionogel binder. Porosity and BET surface area of cathode with ionogel binder is lower than cathode with normal binder due to the swelling of PVDF/IL complex. Ionic conductivity was improved when ionogel binder was employed because Li^+ ion was able to transfer through ionogel binder. The cathodes were employed in Li-O_2/CO_2 battery using 1.0 M LiTFSI in TEGDME as electrolyte. Cathode with [bmim][Tf_2N]/PVDF ionogel binder provides highest discharge capacity at 15.1 mAh cm^{-2}, 3.7 folds higher than cathode with PVDF binder. Moreover, cathode with [bmim][Tf_2N]/PVDF ionogel binder provides higher discharge capacity than Cathode with [bmim][PF_6]/PVDF and [bmim][I]/PVDF ionogel binder. This was explained by solubility of oxygen and carbon dioxide in ionic liquid which was calculated by COSMO-sac method. This shows that ionogel binder improves capacity of Li-O_2/CO_2 battery because of the improvement of ionic conductivity and reaction gases solubility.

Chapter 5 focused on cathode with functionalized ionogel binder for rechargeable Li-O_2 battery. Cathode with PVDF binder, [bmim][Tf_2N]/PVDF ionogel binder and [bmim][I]/PVDF redox mediator-functionalized ionogel binder were fabricated by sc-CO_2 drying at 20.0 MPa, 40℃. The cathodes were assembled with 1.0 M LiTFSI in TEGDME as electrolyte and test with pure O_2. Full discharge-charge profile shows that cathode with [bmim][Tf_2N]/PVDF ionogel binder has largest discharge capacity, while cathode with [bmim][I]/PVDF ionogel binder has lowest discharge capacity. However, cathode with [bmim][I]/PVDF ionogel binder provides smallest overpotential, implying the redox mediator function of cathode by I^- ion from ionic liquid. Cyclability of battery were tested by fixing discharge-charge capacity at 1.0 mAh cm^{-2}. Cathode with [bmim][I]/PVDF ionogel binder shows greatest cyclability among all cathode at stable 18 cycles. X-ray diffraction analysis provided detail of electrochemical route using [bmim][I]/PVDF ionogel binder, which involved the formation of LiOH after discharging and non-reversible $LiIO_3$ after charging. This implies that [bmim][I]/PVDF ionogel binder could be used as redox mediator in cathode, however, non-reversible $LiIO_3$ forming after charging process limited its cyclability.

The conclusion of this work was summarized and stated in chapter 6.