The Modification of Amorphous Manganese Oxide Electrode for Electrochemical Pseudocapacitor

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Electrochemical capacitors have been investigated as an auxiliary unit in a hybrid battery-electrochemical capacitor supply.1 For this purpose, three kinds of electrochemical capacitors have been studied such as Electric Double Layer Capacitor (EDLC), Conducting Polymer Capacitor, and Electrochemical Pseudocapacitor. Briefly saying about these electrochemical capacitors, EDLC, which stores electric energy by physical separation of physisorbed ions on the interface between electrode and electrolyte, has been commercialized. Conducting Polymer Capacitor doesn't show enough performance including cycle life, and Electrochemical Pseudocapacitor, which uses faradic reaction on the electrode surface as well as EDLC mechanism, has paid attention because it is expected theoretically to show better characteristics than EDLC.

This has leaded to the material research for electrochemical pseudocapcitor. Up to now, although amorphous ruthenium oxide is well known as the best example of pseudocapacitive material since it was high specific capacitance and good cycle life, the high cost of material and environmental unfriendliness of electrolyte used hesitates to commercialize it as a pseudocapacitive electrode material. Recently, amorphous manganese oxide has been studied as a new candidate to overcome these problems.²

In the previous study of amorphous manganese oxide, it was investigated the importance of conducting agent and the way of contact between amorphous manganese oxide and conducting agent because of its high intrinsic resistance. Although it was observed from our study that the proper addition of conducting agent could improve the kinetic reversibility, there was the limitation to increase the specific capacitance as higher as the specific capacitance of amorphous ruthenium oxide.³

In this study, the amorphous manganese oxide electrode, including conducting agent of 20 %, was modified to increase capacitance in the volumetric basis. The mixture of amorphous manganese oxide and conducting agent with binder was coated on the substrate. And then a kind of conducting polymer, Polypyrrole (PPY) was electrochemically polymerized to bridge between particles under specific condition. In this work, the normal amorphous manganese oxide electrode which did not include electrochemically polymerized PPY layer showed specific capacitance of 170 F/g, and only PPY electrode showed less than half (82 F/g) of specific capacitance obtained from normal electrode in 0.5 M K₂SO₄. At the same system, the modified amorphous manganese oxide electrode with electrochemically polymerized PPY showed much higher capacitance of 600 F/g in the basis of the weight of amorphous manganese oxide. Actually, it had two times higher specific capacitance as 300 F/g expected from calculation using each specific capacitance of amorphous manganese

oxide and PPY. In the geometric point of view, the amorphous manganese oxide electrode with electrochemically polymerized PPY showed three times higher capacitance of 81 mF/cm² than the capacitance of normal electrode, 26 mF/cm², and good rectangularity of cyclic voltammogram in the range from -0.3 to 0.7 V vs. Ag/AgCl in 0.5 M K_2SO_4 . It disclosed that electrochemical polymerized PPY could contribute to increasing the specific capacitance of amorphous manganese oxide as well as to showing pseudocapacitance because it acted like another conductive path between the particles of amorphous manganese oxide and conducting agent. It was believed to cause the expansion of electron path on the amorphous manganese surface and to increase the number of active sites. The micro spectroscopy of electrode proved that PPY existed not only on the apparent surface of electrode and also between particles.

The modification amorphous manganese oxide electrode for electrochemical pseudocapacitor can be expected highly promising for high capacitance, but it still has poor cycle life problem because of PPY characteristics on the working condition.

References

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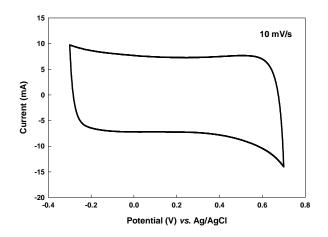


Fig. 1. Cyclic Voltammogram of amorphous manganese oxide electrode with electrochemically polymerized PPY in $0.5M~K_2SO_4$