

New Electrode Materials for Electrochemical Capacitor
-Composite of Porous Carbon with Tungsten Carbide-

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New electrode materials for electrochemical capacitor, composite powders of porous carbon with tungsten carbides, carbon-coated tungsten carbides, were prepared through a simple process. These composite powders gave a high capacitance in 1M H₂SO₄ electrolyte.

The starting materials used were hydroxyl propyl cellulose (HPC) as carbon precursor and K₂WO₄ powder of reagent grade as the precursor for tungsten carbides. Two precursors were dissolved into water in an equal mass ratio. The precursor solution thus prepared became gel at room temperature. This gel was dried in vacuum and then heat-treated at a temperature between 800 and 1050°C for 1h under Ar atmosphere. After the heat treatment, the powders obtained were washed by 1M H₂SO₄ and distilled water in order to dissolve out the potassium metal which might be remained in the powders.

X-ray diffraction patterns of the powders prepared at different temperatures are shown in Fig.1. Above 850°C, two kinds of tungsten carbides W₂C and WC are formed, together with metallic W. With increasing temperature, relative intensities of the diffraction peaks for WC increase, suggesting the following reaction processes: the decomposition of carbon precursor HPC to carbonaceous materials, the decomposition of the precursor K₂WO₄, the reduction of tungsten oxide by the carbonaceous materials to W₂C and finally to WC. These carbide particles were observed carbon-coated state by TEM, and its size was approximately 50nm. In Fig. 2, carbon content, which was determined from the ignition loss at 470°C in air, and BET surface area are plotted against heat treatment temperature. Carbon content decreases monotonically with increasing temperature, probably due to the consumption of carbon for the reduction of tungsten oxides. The powders prepared above 1000°C show relatively large BET surface area as about 170m²/g, showing the formation of highly porous carbons. The abrupt increase in BET surface area observed is supposed to be activation by the vaporized potassium from K₂WO₄.

The electrochemical performance of the composite was studied by cyclic voltammetry and galvanostatic charge-discharge cycles in three electrodes cell in 1M H₂SO₄ electrolyte. CV curve observed on the powder prepared at 1000°C (Fig. 3) is box-shape and gives the capacitance of 210F/g (at 0.5V). In the powders recovered after the first charge-discharge cycle, tungsten hydroxide was detected from XRD, but no tungsten carbides.

The powders prepared in the present work were the composite of tungsten carbides with porous carbon, *i.e.*, carbon-coated tungsten carbides. Changes from carbides to hydroxides of tungsten are completed within the first cycle of charge-discharge because of fine particles. Porous carbon coated on tungsten carbides may avoid the growth of tungsten carbides during their formation and the agglomeration of tungsten hydroxides during charge-discharge cycles, as well as act as electrode materials for electric double-layer capacitor.

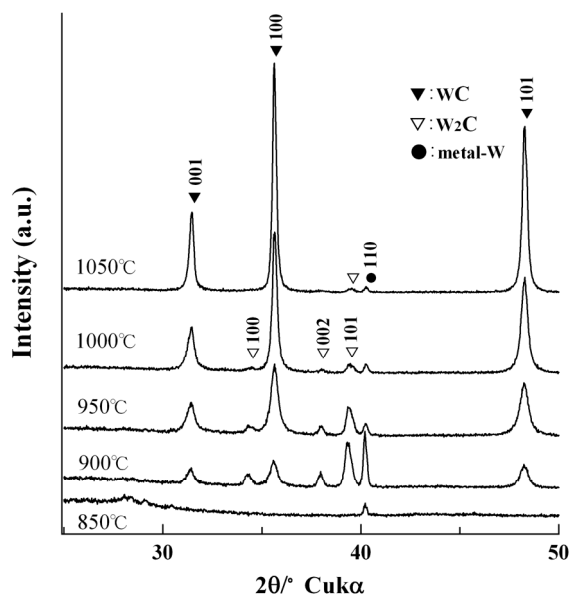


Fig. 1 XRD patterns of powders obtained under different synthesized temperature.

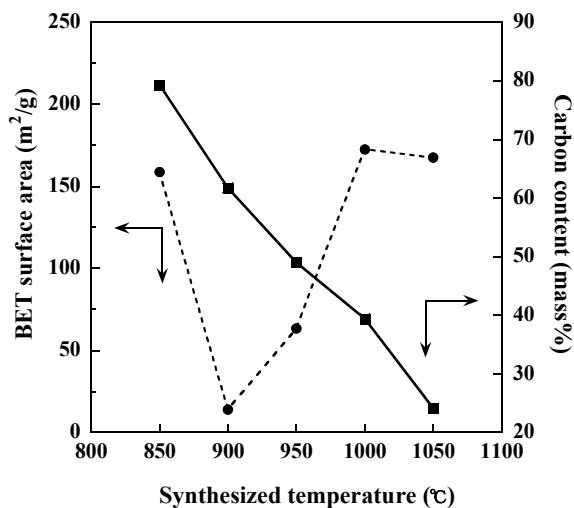


Fig. 2 Changes in carbon content and BET surface area of the composite powders with synthesis temperature.

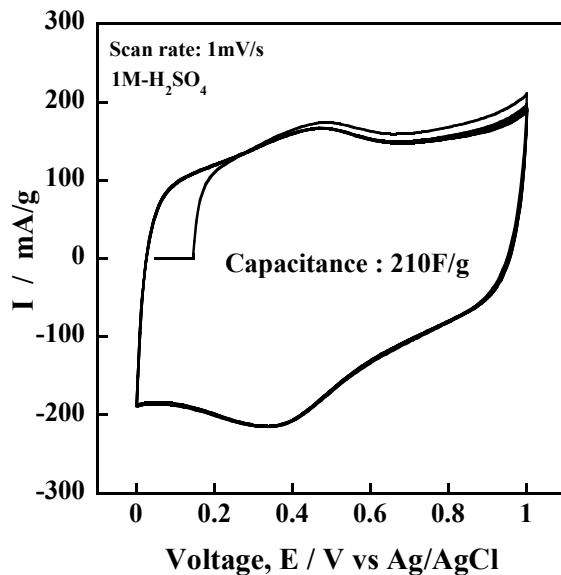


Fig. 3 Cyclic voltammogram of porous carbon coated tungsten carbide prepared at 1000°C.