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1. General Introduction

Electrochemical capacitors (ECs) store energy using either ion adsorption (electrochemical double-layer capacitors) or fast surface redox reactions (pseudocapacitors). ECs are considered as one of the key energy storage devices owing to their much higher power density and longer lifetime than those of secondary batteries, but their applications field is still limited by their relatively low energy density. In principle, a large energy density can be achieved by increasing both the capacitance of an electrode and its working voltage. The capacitance generally depends on the physical properties of electrode materials such as specific surface area, pore structure, graphene curvature and surface chemistry. The working voltage is governed by electrolytes and the reactivity of the electrode materials, such as an amount of edge sites of carbon materials. In this thesis, zeolite-templated carbon (ZTC), which is a high-surface microporous carbon, is chosen as a starting material and its structural control to achieve high performance ECs is investigated. ZTC is synthesized as a negative replica of zeolite Y template, and has an interesting carbon framework, i.e. buckybowl-like framework structure (Fig. 1), containing a lot of edge sites. In Chapter 2, ZTC framework is changed from its intrinsic buckybowl-like structure (Fig. 1) to crosslinked-fullerene-like structure (Fig. 2) in order to realize positive curvature, which is expected to have higher capacitance [1]. Moreover, a less amount of edge sites of this structure would be beneficial for expanding the working voltage. On the contrary, in Chapter 3, ZTC with the buckybowl-like structure is utilized by taking the advantage of its large amount of edge sites, in which a large amount of redox-active functional groups can be introduced. Finally in Chapter 4, considering the redox reaction of ZTC at positive potential range, an asymmetric capacitor is constructed using ZTC and stable activated carbon as a positive and negative electrodes, respectively, in a sulfuric acid electrolyte.

2. Fullerene-Like Carbon Framework – A New Form of $sp^2$ Carbon –

Huang et al. [1] has reported that carbon with a nanotube- or fullerene-like frameworks, would exhibit an interestingly high capacitance, according to exohedral interaction of the ions on the external surface of carbon framework. In this chapter, we report the formation of a three-dimensional fullerene-like framework that can be considered as a new carbon allotrope by introducing a large
amount of carbon into the confined nanochannels of zeolite Y using a pulsed CVD technique. It is found that the carbon deposition takes place not only inside the zeolite nanochannels but also on the outer surfaces of zeolite particles, resulting in the formation of a thick carbon shell. These two different carbons have different reactivities toward O\textsubscript{2} oxidation and it is able to use this difference to determine the amount and the elemental composition of the inner carbon portion, which corresponds to the carbon deposition inside the zeolite nanochannels. An average composition of the replicated carbon is C\textsubscript{63}H\textsubscript{4.9}O\textsubscript{1.2}, which is very close to that of fullerene C\textsubscript{60}. Additionally, a wavelength-dispersive soft-X-ray emission spectroscopy reveals that its valence electron structure is distinct from any conventional sp\textsuperscript{2}-based carbon materials, and has similarities to that of fullerene C\textsubscript{60}. As a possible structure for the present nanocarbon network, a crosslinked-fullerene-like framework with the same three-dimensional regularity (Fig. 2) is proposed [2]. Such a framework is close to carbon schwarzite (a three-dimensional graphene-based framework), which is an as-yet-unsynthesized hypothetic material. The present new material is expected to have specific physical properties, as suggested by its unique valence electron structure. However, its normalized capacitance (F m\textsuperscript{-2}) does not significantly differ from those of commercial activated carbons, against the aforementioned prediction. Additionally, the working potential was not significantly increased regardless a less amount of edge sites compared to the ZTC with a buckybow-like structure.

3. Electrochemical-Functionalization of Zeolite-Templated Carbon

ZTC (Fig. 1) contains a lot of highly reactive edge sites, which are easily electrooxidized to be functionalized by redox reactive quinone groups in sulfuric acid electrolyte [3]. We demonstrate in this chapter that ZTC shows unique polarization behavior also in an organic electrolyte (1 M Et\textsubscript{4}N-BF\textsubscript{4} in PC), compared to activated carbons (MSC30). Cyclic voltammograms of MSC30 and ZTC were measured in –1.5 to 1.0 V (Ag/Ag\textsuperscript{+}). MSC30 showed a typical rectangular shape, indicating its electric double-layer capacitance. On the other hand, ZTC showed two redox couples around –0.8 and 0.4 V, indicating the significant contribution by pseudocapacitance. Additionally, towards the negative potential polarization, another redox peak around –1.2 V was observed. Temperature-programmed desorption and FT-IR analyses indicated that the origin of the pseudocapacitance would be oxygen-functional groups corresponding to CO-evolution groups (acid anhydride, ether, phenol, and/or quinone), which were introduced by the polarization. In order to clarify the key functional group, we have prepared quinone-functionalized ZTC by the method which was previously developed by us, and examine its cyclic voltammogram: the quinone-functionalized ZTC showed similar redox peaks as the aforementioned oxidized ZTC in the organic electrolyte. It is thus confirmed that the quinone groups are introduced into ZTC by the polarization in the organic electrolyte, and they exhibit the large pseudocapacitance. The optimized potential window of ZTC in this electrolyte is –2.0 ~ 1.0 V (vs. Ag/Ag\textsuperscript{+}), and ZTC shows a high specific capacitance ranging from 230 to 330 F g\textsuperscript{-1}, which are higher than those of MSC30 (180-250 F g\textsuperscript{-1}), together with an excellent cyclability. Consequently, ZTC is expected as a potential pseudocapacitive electrode material for ECs.

4. Asymmetric Aqueous Capacitor Using Pseudocapacitive ZTC as One of the Electrodes

This chapter demonstrates more practical EC cell configuration using ZTC as an electrode material. Although most of commercial EC products utilize the organic electrolytes presently, environmental-friendly aqueous electrolytes offer an attractive advantage of high ionic conductivity, which enhances the power density. ZTC exhibits a large pseudocapacitance in the aqueous electrolyte (sulfuric acid) but only in a positive potential region. Therefore, an asymmetric capacitor assembled by ZTC as a positive electrode and KOH-activated (AC) carbon as a negative electrode is designed and characterized in the sulfuric acid electrolyte. Thanks
to the contribution by the pseudocapacitance of ZTC at positive potential and good stability of AC at negative potential, the asymmetric capacitor exhibits higher capacitance than symmetric capacitors prepared from ZTC or AC alone (Fig. 3), with a relatively wide potential window of 1.4 V as an aqueous system. Moreover, it shows a good cyclability with high capacitance retention during 5000 cycles of the durability test. The asymmetric ZTC/AC capacitor exhibits high energy density (24.5 Wh kg\(^{-1}\)), which is comparable to those of AC/AC symmetric capacitors utilizing the organic electrolytes. This chapter proves that it is possible to construct asymmetric aqueous capacitors having comparable performance to conventional organic capacitors, by using the pseudocapacitive ZTC together with the stable AC.

5. Concluding Remarks

Two different approaches were examined on the structure modification of ZTC to realize a high-performance electrode material for ECs. The first approach, decreasing the edge sites of ZTC, was found not to be effective way. However, the resulting material, i.e., crosslinked-fullerene-like framework structure, is a new class of \(sp^2\)-carbon based material which is expected to future researches. The second approach, utilization of the large amount of reactive edge site, was revealed to be an interesting way to enhance the capacitance from a contribution of electrochemically-introduced functional group. Additionally, this thesis establishes the method to constructing more practical EC cell using pseudocapacitive ZTC as an electrode material.

論文審査結果の要旨

電気化学キャパシタはイオンの吸着あるいは表面における迅速な酸化還元反応（疑似容量）により電荷を蓄えるデバイスであり、高いバリ密度と長い寿命が特長である。しかし、エネルギードライバ密度が低いことが欠点であり、このことが応用の限界を狭めている。エネルギードライバ密度を上げるためには容量そのものを高め、さらに作用電位を広げることが効果的である。容量は電極炭素材料の表面積、細孔構造、グラフェンの曲率、表面化学に依存しており、作用電位は電解質の種類、電極材料の反応性が重要なパラメータになる。本論文ではゼオライト型炭素を対象物質として、その構造を制御することで高いエネルギードライバ密度をもつ電気化学キャパシタにすることを目指した研究であり、5つの章から構成される。

第1章は緒言であり、本研究の背景、従来の知見、研究目的および意義について述べている。

第2章ではゼオライト型を利用することでフラークレーンがネットワーク状に規則的に連結したような構造の炭素材料の合成を試みた。ナノチューブやフラーレンのような曲面の外側にイオンが吸着すると非常に高い容量を示すことが理論的に予想されている。そこで、このような構造の炭素を得るためにパルスCVD法によりゼオライトの細孔中を出来るだけたくさんの炭素原子の充填を試みた。その結果、ゼオライトスーパーケージ当たり平均分子式としてC_{60}H_{48}O_{13}もこの炭素が合った。この分子式はフラークレーンと近い。さらに軟X線発光分析よりも合成した炭素の強電子帯の電子構造は黒鉛よりも類似したフラークレーンに近いことが明らかとなった。以上の結果から合成した炭素は目的のフラークレーンがネットワーク状に規則的に連結したような構造になっていることが分かった。しかし、この炭素のキャパシタ特性を完全に評価したところ、性能の大幅な向上は見られなかった。

第3章ではゼオライト型炭素に含まれた量のエッジサイトを電気化学的に活性化することで容量の増加を狙った。有機電解質中でゼオライト型の炭素を製造するかは選択的に分極しているところ、どちらの場合も一度分極すると分極以前にはなかった数値曲線が発現した。昇温脱離法およびFT-IRで分析を行うと、数値曲線の形状を比較して生成した含酸素官能基によって生じていることが分かった。分極程度を最適化するとゼオライト型炭素は330 F g^{-1}もこの巨大な容量を発揮することが明らかとなった。

第4章ではゼオライト型炭素を電極として用いた実用的なキャパシタシステムの構築を行った。ここでは電極に用いる高イオン導通性が期待できる水溶液系の電解質を使用した。ゼオライト型炭素は酸性電極では凝縮性が高い容量を示すが、酸性電極では凝縮性が高い電極では酸性電極が有利である。そこで、ゼオライト型の炭素を電極、化学的に安定した活性炭を作り、その性能を調べてみた。その結果、非対称キャパシタは通常の対称キャパシタよりも高い容量を示し、サイクル性も良好であった。また、電位電流も広いのでこの非対称キャパシタのエネルギー密度は24.5 Wh kg^{-1}も高い値となった。この値は通常の有機系電解質を用いた活性炭キャパシタに匹敵する。

第5章では結論であり、研究全体の総括を行っている。以上、本論文ではゼオライト型炭素の分子構造を精密に制御することでフラークレーンがネットワーク状に規則的に連結した今までにない新しい形態を作り出すことに成功し、さらにゼオライト型炭素を制御することで電気化学キャパシタ用電極材料として極めて高いエネルギードライバ密度をもつことを実証したものであり、材料科学の発展に寄与するところが多い。

よって、本論文は博士(工学)の学位論文として合格と認める。