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## 論文内容要旨

### Chapter 1: General Introduction

Supercapacitor is an energy storage device known for its high power density and long cycling life. While supercapacitors are used in some electric devices and electric vehicles, the application fields are relatively limited compared to secondary batteries. To extend supercapacitor applications, it is desired to increase stability of supercapacitors. By increasing stability, the working voltage of supercapacitors can be increased, and thus, the energy density is also improved. Moreover, the increase of working voltage is important for reducing the cell stacking number in large modules to output high voltage. It is generally anticipated that supercapacitor degradation is caused by the electrolyte decomposition<sup>1</sup> and carbon corrosion<sup>2</sup>. Thus, understanding degradation mechanisms both at electrolyte and carbon sides are crucial. As for the electrolyte decomposition, previous studies applied very harsh conditions, and it has been still not clear which component in electrolytes is decomposed at an initial degradation stage. As for the effect of the carbon side, only limited investigation has been done using limited types of carbon materials, and moreover, there has been no quantitative discussion regarding the relation between specific carbon structures and the degree of corrosion reactions. One of the reasons for such a situation is the fact that the structure of carbon materials is too complex to be characterized, and there was no appropriate method to quantitatively characterize carbon edge sites. In Chapter 1, the background mentioned above is summarized and the present state-of-art as well as remaining problems are explained. In Chapter 2, systematic investigation is performed using advanced analysis techniques and a variety of different carbon materials to figure out the degradation mechanisms of supercapacitor at a positive potential range. The developed methodology is applied also to a negative potential range in Chapter 3. In Chapter 4, an intrinsic problem in the carbon-edge characterization is pointed out, and an alternative method is proposed. Chapter 5 summarizes this thesis. Through this study, many new findings have been revealed about the degradation mechanisms of supercapacitors.

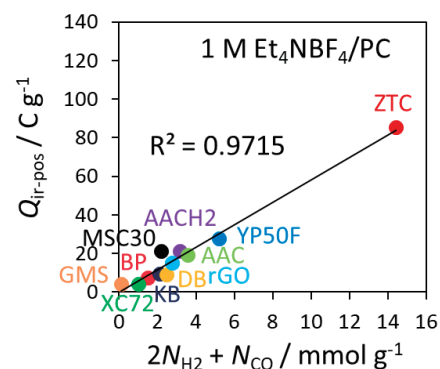
## Chapter 2: Degradation in Positive Potential Range

To reveal reactant(s) at the electrolyte side, electrolyte salt ( $\text{Et}_4\text{NBF}_4$ ) and electrolyte solvents (PC or AN) were individually mixed with a stable ionic liquid (trimethylpropylammonium bis (trifluoromethanesulfonyl) imide) which functions as an inert background, and the reactivities of these components were examined by cyclic voltammetry (CV). As a result, it has been revealed that electrolyte solvents (PC or AN) are more reactive than salt ( $\text{Et}_4\text{NBF}_4$ ) at the positive potential range.

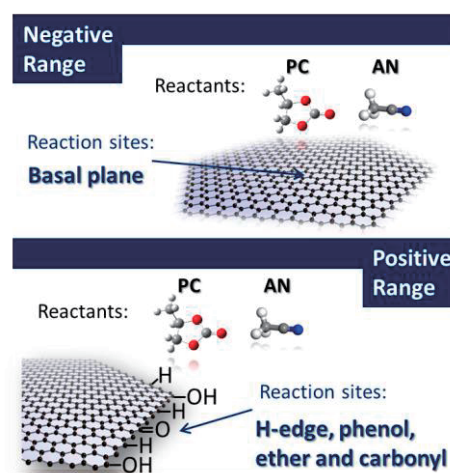
For the understanding of carbon reaction sites, eleven carbon materials including activated carbons, carbon blacks, reduced graphene oxide (rGO), zeolite template carbon (ZTC) and graphene mesosponge (GMS) were investigated. By using these very different carbon materials, a common structural factor(s) affecting supercapacitor degradation is discussed. The carbon materials were characterized by nitrogen adsorption/desorption, X-ray diffraction, Raman spectroscopy, magnetic susceptibility measurement and advanced temperature-programmed desorption (TPD) method. It should be noted that the upper limit temperature of conventional TPD is no more than 1200 °C, which is not high enough to quantitatively analyze H-terminated edge sites. The advanced TPD used in this work can reach 1800 °C at which all the carbon edge sites terminated by O or H can be thermally decomposed and quantitatively detected.<sup>3</sup> By these techniques, a full picture of carbon structure can be obtained. The electrochemical degradation on these carbons was examined with CV by stepwisely expanding its scanning potential range. The degree of the degradation was quantitatively evaluated by the electric charges ( $Q_{\text{ir-pos}}$ ) associated with irreversible degradation reactions during the CV scans at the positive potential range. It is found that carbon porosity, crystallinity and the number of radicals have almost nothing to do with degradation, while a linear correlation is found between  $Q_{\text{ir-pos}}$  and the amount of  $\text{H}_2$  ( $N_{\text{H}_2}$ ) and CO ( $N_{\text{CO}}$ ) gases desorbed during TPD (Figure 1). Thus, H-terminated edge sites, phenol, ether and carbonyl are found to be the reaction sites on carbon materials at the positive potential range.<sup>4</sup>

## Chapter 3: Degradation in Negative Potential Range

The methodology developed in Chapter 2 was applied to a negative potential range. To reveal reactant(s) at the electrolyte side,  $\text{Et}_4\text{NBF}_4$ , PC, or AN was individually mixed with a stable ionic liquid (1-Butyl-3-methylimidazolium tetrafluoroborate) which functions as an inert background. The mixture electrolytes thus prepared were characterized by CV. Similar to the case of the positive potential range, electrolyte solvents (PC or AN) are found to be more reactive than salt ( $\text{Et}_4\text{NBF}_4$ ) at the negative potential range.



**Figure 1**  $Q_{\text{ir-pos}}$  (1.0 V vs.  $\text{Ag}/\text{AgClO}_4$  in 1 M  $\text{Et}_4\text{NBF}_4/\text{PC}$ ) versus the sum of the TPD  $\text{H}_2$  and CO evolutions.

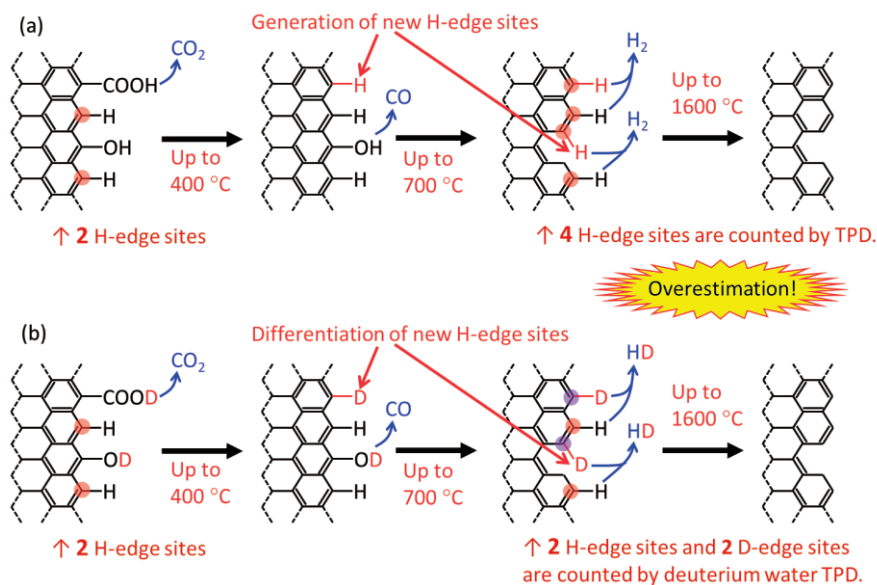


**Figure 2** Illustration of reactants and reaction sites in negative and positive potential range, respectively.

For the understanding of carbon reaction sites, eight different carbon materials including activated carbons, carbon blacks, ZTC and GMS were investigated. The carbon properties were characterized by nitrogen adsorption/desorption and TPD. The total surface area determined by the nitrogen adsorption measurement was divided into basal-plane surface area ( $S_{\text{basal}}$ ) and edge-plane surface area ( $S_{\text{edge}}$ ) by using the results of these two techniques. The electrochemical degradation on these carbons was quantitatively evaluated by the electric charges ( $Q_{\text{ir-neg}}$ ) associated with irreversible degradation reactions during CV scans at the negative potential range. Unlike the case of the positive potential range, it is found that  $Q_{\text{ir-neg}}$  has no correlation with the amount of carbon edge sites. Interestingly, a linear correlation is found between  $Q_{\text{ir-neg}}$  and  $S_{\text{basal}}$ . Thus, the experimental results suggest that carbon degradation mainly occurs on carbon basal plane at the negative potential range (Figure 2). The reaction mechanism was further supported by a theoretical calculation.

#### Chapter 4: Effect of Carbon Surface Modification on the Stability of Supercapacitors in Positive Potential Range

Although specific edge sites including H-terminated edge sites, phenol, ether and carbonyl are found to be reactive at the positive potential range, the reactivity of each site is not revealed due to the small amounts of oxygen functional groups on carbons investigated previously (Chapter 2). Thus, a commercial activated



**Figure 3** The scheme of the edge-structure transformation during TPD measurement. (a) Conventional carbon. (b) Carbon pre-treated by  $D_2O$  for exchanging H in  $-OH$  and  $-COOH$  with D.

carbon YP50F was chemically oxidized by nitric acid to introduce a large amount of oxygen functional groups. Also, the types of oxygen-functional groups were controlled by a post heat-treatment. In these oxygen-rich carbon materials, the amount of H-terminated edge sites is overestimated by the TPD technique because carboxyl and phenol can be thermally decomposed as  $CO_2$  or  $CO$  gases but leave new H-terminated edge sites during the measurement. The newly generated H-terminated edge sites cannot be distinguished from the original H-terminated edge sites by TPD and cause overestimation (Figure 3a). In order to precisely characterize the H-terminated edge sites, these carbons were immersed in deuterium water to exchange the H atoms of carboxyl or phenol groups with D atoms. By this procedure, the newly formed D-terminated edge sites due to the decomposition of oxygen functional groups can be distinguished from the original H-terminated edge sites and therefore the overestimation can be avoided (Figure 3b). It is found that at 1.3 V vs.  $Ag/AgClO_4$ , these intentionally modified carbon materials matches the previous conclusion on various carbons very well, further proving that H-terminated edge sites, phenol, ether and carbonyl are active sites at positive potential range. However, at 1.0 V vs.  $Ag/AgClO_4$ ,  $Q_{\text{ir-pos}}$  is more related to H-terminated edge sites, which suggests that some parts of phenol, ether or carbonyl are not reactive at lower potential range. Thus it is concluded that H-terminated edge sites are more reactive than oxygen functional groups at lower potential range.

## Chapter 5: Conclusions and Perspectives for Further Research

This thesis systematically investigated the electrochemical degradation mechanism of supercapacitors with organic electrolytes of Et<sub>4</sub>NBF<sub>4</sub>/PC or Et<sub>4</sub>NBF<sub>4</sub>/AN. In Chapter 2, the origin of degradation in positive potential range has been explored. The reactants in the electrolyte are found to be electrolyte solvents (PC or AN) rather than salt (Et<sub>4</sub>NBF<sub>4</sub>). The reaction sites on carbon materials are confirmed as H-terminated edge sites, phenol, ether and carbonyl on carbon edges, and carbon porosity, crystallinity or radicals do not have any correlation with electrochemical degradation. In Chapter 3, the degradation mechanism in negative potential range has been examined. Similar to the case of the positive potential range, electrolyte solvents (PC or AN) are found to be more reactive than salt (Et<sub>4</sub>NBF<sub>4</sub>) at the negative potential range. However, the degradation reactions mainly occur at the carbon basal planes rather than the edge sites, which makes a striking contrast to the positive potential case. In Chapter 4, the reactivities of carbon edge sites at positive potential range have been investigated. It is found that H-terminated edge sites are more reactive than oxygen functional groups at lower potential range. This work demonstrates that a combination of CV and TPD is useful for a molecular understanding of electrochemical process, which is also promising for studying supercapacitors using aqueous or ionic liquid electrolyte.

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# 論文審査結果の要旨

スーパーキャパシタは高パワー密度でかつ長寿命のエネルギー貯蔵デバイスである。しかし、電気化学的劣化を防ぐため作動電圧が小さく、エネルギー密度が低い。そのため、二次電池と比較してスーパーキャパシタの応用用途は限られており、高電圧でも劣化しないスーパーキャパシタを作製することは工業的に重要である。スーパーキャパシタの電気化学的劣化は電解液と接触している炭素表面で起こるが、包括的な研究が一切されていないのが現状である。この理由は炭素表面そのものが非常に複雑で科学的な理解が難しいことにつきる。そこで、本研究では種類の異なる多数の炭素材料を電極として使用し、それら炭素材料の構造分析を徹底的に行い、有機電解液の電気化学的劣化反応が炭素表面のどのようなサイトで起こっているかを明らかにしようとした研究であり、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章ではスーパーキャパシタの正極側での電気化学的劣化反応について検討した。電極として活性炭、カーボンブラック、還元型酸化グラフェン、ゼオライト鋳型炭素、グラフェンメソスポンジ等、計11種類の炭素材料を使用した。有機電解液としては塩 ( $\text{Et}_4\text{NBF}_4$ ) のポリカーボネート(PC)あるいはアセトニトリル(AN) 溶液を用い、3極式セルにて正極側での電気化学的劣化過程を測定した。使用した炭素を様々な方法で徹底的に分析し、その構造パラメーターと劣化の程度との関係を調べた。その結果、正極側での劣化は炭素の表面積や結晶性、スピン濃度等とは関係なく、昇温脱離法で調べた水素終端のエッジサイト数とカルボニル基、フェノール基等の数との合計と強い正の相関があった。つまり、正極側ではこれらのエッジサイトと溶媒 (PC あるいは AN) との反応で劣化が起こっていることを明らかにした。

第3章ではスーパーキャパシタの負極側での電気化学的劣化反応について検討した。その結果、負極側での劣化は炭素のエッジサイトの数とは全く関係なく、炭素の全表面積と相関があった。そこで、全表面積を炭素ベーサル面とエッジ面の2つに分けて解析したところ、劣化の程度は炭素のベーサル面の面積と強い相関があり、負極側では PC、AN とも劣化反応は炭素ベーサル面上で起こっていることを明らかにした。さらに、分子軌道法を用いて炭素ベーサル面とエッジ面における溶媒の反応を解析したところ、ベーサル面の方が溶媒への電子供与が起こりやすいことを理論的にも明らかにした。

第4章では正極側での電気化学的劣化反応について表面を化学修飾した活性炭を用いてさらに詳しく解析し、各エッジサイトの反応性について議論した。スーパーキャパシタとしての実際の使用では負極側より正極側での劣化が大きな問題である。そこで、湿式酸化や熱処理等により表面含酸素官能基量の大きく異なる活性炭数種類を調製し、正極側での電気化学的劣化反応を調べた。まず、表面含酸素官能基量の多い活性炭では水素終端のエッジサイトの数が昇温脱離法では過大評価されるので、重水素を利用することでその補正を行った。次に補正したエッジサイトの量と正極側での劣化の程度を比較した。その結果、水素終端のエッジサイトの反応性がエッジにある表面含酸素官能基より高いことが明らかになった。

第5章は結論であり、研究全体の総括を行っている。

以上、本博士論文では、種類の異なる多数の炭素材料を電極として使用しスーパーキャパシタにおける電気化学的劣化反応について初めて系統的な解析を行い、正極側と負極側で劣化反応が起こる炭素のサイトが異なることを実証し、さらに各サイトの反応性も異なることを明らかにしたものであり、材料化学及び電気化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。