# Development of a CVD-based Technique for Homogeneous Deposition of $TiO_2$ Nanoparticles inside the Pores of a Porous Carbon Substrate

Shinichiroh Iwamura*, Shota Motohashi, Shin R. Mukai

[1]*Affiliation1: Faculty of Engineering. Hokkaido University, Sapporo, Japan*

*Presenting author's e-mail: iwamura@eng.hokudai.ac.jp

## Introduction

$TiO_2$ is an attractive material for photocatalyst and electrode applications. When $TiO_2$ is used as an anode material in lithium-ion capacitors (LICs), metal Li deposition and electrolyte decomposition hardly occur, which usually reduce rate and cycle performance of typical graphite anodes. Thus, $TiO_2$ is one of candidate materials for high performance LICs. The utilization of $TiO_2$ requires the combining of it with a carbon material to improve its electrical conductivity and the nano-sizing of it to increase the surface area contacting with the reactant or electrolyte. While various $TiO_2$/C nanocomposites were reported, the production of these nanocomposites requires expensive initial materials and/or high-costs for processing. Thus, it is difficult to industrially produce such nanocomposites using methods reported so far. Considering the industrial production, $TiO_2$ deposition on a commercially-averrable carbon material using a chemical vapor deposition (CVD) technique is an attractive way, where Ti source vapor is thermally decomposed into $TiO_2$ on the carbon material. However, most of Ti source materials have too high reactivity or low vapor pressure to homogenously deposit $TiO_2$ nanoparticles by typical CVD techniques. In this study, the vacuum liquid pulse chemical vapor deposition (VLP-CVD) technique was developed for the efficient production of $TiO_2$/porous-carbon nanocomposites. In this technique, a porous carbon was heated in a tubular reactor under vacuum and a Ti source was injected into it as liquid pulses. Then, the Ti source vapor can be smoothly distributed into the pores of the porous carbon before its thermal decomposition, and $TiO_2$ nanoparticles with a small diameter are formed inside the pores. Through this technique, $TiO_2$/C nanocomposites were prepared using porous carbon materials with various pore size, and their anode performance was evaluated.

## Materials and Methods

A perpendicular tubular reactor setting with a glass filter at its center was used. A macroporous carbon (average pore size: 150 nm, C(150)) was placed on the glass filter, and titanium tetraisopropoxide was injected as liquid pulses (50 µm/pulse) into the reactor heated to 180°C under vacuum conditions. After the pulse injection was repeated 100 times, the sample was heat-treated at 700°C for 1 h under a $N_2$ flow. For comparison, continuous-flow CVD and continuous vacuum CVD were also conducted by continuously introducing the Ti source under a $N_2$ flow and vacuum, respectively.

The samples were analyzed via thermal gravimetric (TG) analysis under an air flow, and transmission electron microscopy (TEM). The anode performance was evaluated through galvanostatic charge/discharge measurements using a three-electrode cell with an metal Li reference and counter electrode, and 1 M $LiPF_6$ EC/DEC electrolyte.

## Results and Discussion

Figure 1 shows the TEM images of the C(150) and $TiO_2$/C nanocomposites prepared by the various CVD using C(150). Note that $TiO_2$ content of each composite was determined to be ca. 40 wt% by TG analysis. The images of the composites prepared by the continuous-flow and vacuum CVD show that the particle size of the deposited $TiO_2$ nanoparticles were larger than 10 nm. In contrast, the image of the composite prepared by the VLP-CVD indicates that the VLP-CVD enables homogeneous deposition of $TiO_2$ nanoparticles with a diameter of around 4 nm through the entire porous carbon substrate.

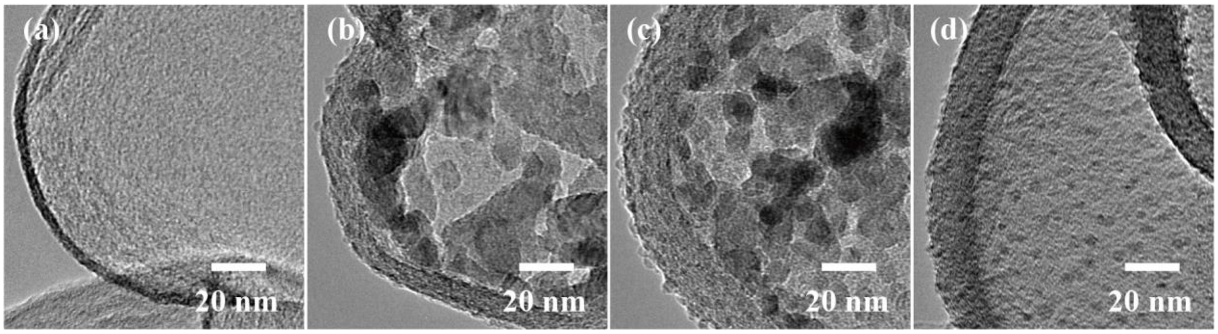


**Figure 1. TEM images of (a) C(150) and $TiO_2$/C nanocomposites prepared from it by the (b) continuous-flow CVD, (c) continuous-vacuum CVD, and (d) VLP-CVD.**

To investigate the relationship between the deposition state of $TiO_2$ and the anode performance, electrochemical measurements were conducted. Figure 2 shows the discharge capacities of the samples prepared by each CVD measured at various current densities. The discharge capacities of the sample obtained by the VLP-CVD at low current densities were ~10 mAh/g higher than those of samples prepared by the continuous CVD. At a current density of 5000 mA/g, the discharge capacities of the samples prepared by the VLP-CVD and continuous CVD were 50 and 20 mAh/g, respectively. These results indicate that the small $TiO_2$ nanoparticles deposited by the VLP-CVD had a large surface area that was in contact with the electrolyte and effectively produced a conductive path in carbon.

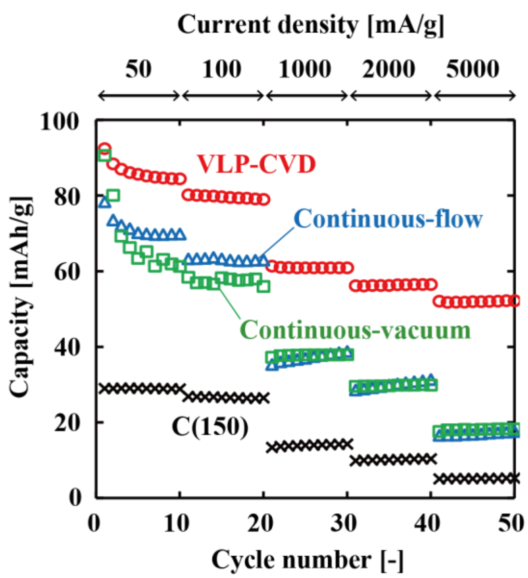


**Figure 2. Discharge capacities of C(150) and $TiO_2$/C nanocomposites prepared through various CVD techniques, measured at various current densities.**

## Conclusions

$TiO_2$ nanoparticles with a diameter of 5 nm were homogeneously deposited inside pores of the macroporous carbon through the VLP-CVD technique. By utilizing the small diameter of $TiO_2$ nanoparticles and the homogeneous electrically conductive path, the obtained $TiO_2$/C nanocomposites can be used as electrode materials having high rate performance.

## Acknowledgment

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