

CARBON MATERIALS EMBEDDED WITH METAL NANOPARTICLES AS ANODE IN LITHIUM-ION BATTERIES

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Introduction

Metals that can form alloy with lithium may be used as anode in Lithium-ion batteries. They generally have high lithium-storage capacity. However, their cycle lives are short, possibly due to the volume changes and the resulted disintegration during alloy formation.

For long cycle life anodes, carbon materials were used. The long cycle life is a result of SEI (surface electrolyte interface) formation on the carbon surface during the first cycle of lithium insertion. The SEI protects the carbon interior during the later cycles. However, carbon's capacity to store lithium is lower than the typical metals used for this purpose.

It is proposed in this study that a carbon material containing metal nanoparticles that can form alloy with lithium may have the advantages of both the metal and the carbon material. Metal provides the additional lithium storage capacity, and SEI on the carbon surface protect both the carbon interior and the metal particles, while voids in the carbon interior accommodate the volume changes of the nanoparticles during the lithium alloy formation.

This potential advantage of adding metal nanoparticles into carbon electrode has been studied and is demonstrated in this report.

Experimental

Carbon fibers containing palladium nanoparticles were fabricated by exposing fluorinated fibers to a mixture of PdCl₂ and CuCl₂ in nitrogen environment, followed by heating in N₂ at 1100°C. Details of this process was described previously [1]. Its composition was estimated to be, by mass, 34% carbon, 59% palladium, 5% copper and 2% chlorine. The empirical formula was therefore C₅PdCu_{0.15}Cl_{0.1}. It x-ray diffraction data indicated the presence of Pd and a small amount of PdCu₃. The sizes of the Pd particles were not measured. However, TEM data on similarly treated samples indicated most particles were in the 20-1000 Å range.

For convenience, the above sample of carbon containing palladium is labeled C(Pd) in this report. The carbon portion of this sample without the presence of Pd cannot be obtained. However, it is chemically similar to another carbon sample that was made previously from the same precursor by the same method except the metal chlorides were replaced by C₄H₄Br₂ during the fabrication process. This carbon fiber is labeled as C(0) in this report.

The fibers were tied to one end of a thin nickel string. The other end of the string was tied to a nickel rod, which was the electrode of a half cell, C(Pd)/0.5MLi-50/50 (vol%) EC and DMC/Li, using Li metal as the reference electrode. No binder was used for the C(Pd) electrode.

Electrochemical test was performed using constant current (10 mA/g) to insert and release the C(Pd) sample for 3 cycles between 0 and 2.5 V, followed by 4 cycles between 0 and 0.4V. The voltages difference between the working electrode and reference electrode (V_{wr}) was recorded once in every five minutes.

The electrochemical data for the C(Pd) sample described above were compared to those for its precursor (graphitized carbon fibers P-100) and the carbon fibers C(0) described above.

Results and Discussions

Figure 1 shows the voltages (V_{we}) of the C(Pd), C(0), and their precursor as functions of charge-discharge capacity (Q) during the first cycle of lithium insertion and release. This figure indicates that the capacity for the C(Pd) sample was larger than that for either the same carbon without the presence of Pd particles, C(0), or their precursor. Specifically, the sample made of 1 g composite (0.34g C, 0.59g Pd, and 0.07g other elements) had a higher capacity than the sample of 1 g carbon, where the carbon in both samples had similar chemical properties. Pd was clearly an active element of lithium storage.

The voltage range during which Pd nanoparticles were reactive to lithium can be observed in Figure 2, where dQ/dV_{wr} is plotted against V_{wr} for lithium release reaction. Comparing the plot for C(P) and C(0), it can be seen that the Pd-Li reaction occurred mostly when $V_{wr} < 75$ mV.

Interestingly, there were no sharp peaks for Pd-Li reaction, possibly because the Pd particles were too small to have normal bulk Pd properties.

Another observation from Figure 2 was the presence of peaks representing lithium intercalation in carbon (80, 120, and 180 mV). This indicates that the carbon in this sample can still intercalate with lithium, even though it already contained a large amount of Pd.

Table 1 shows the capacity of C(Pd) for every half cycle during the entire experiment of 7 cycles. After 3 cycles of lithium insertion and release in 0 to 2.5V range, the capacity of lithium insertion approached the capacity of lithium release. However, it appears that the capacity continued to decrease as more cycle of insertion and release were performed. A further examination of the V_{wr} -capacity curves concluded that such decrease was the result of capacity loss at high voltage range ($0.4V < V_{wr} < 2.5V$). Because of this, the subsequent 4 cycles were performed in 0 to 0.4V range. After such adjustment, the

capacity loss disappeared. This suggests that the C(Pd) sample may have a long cycle life.

Conclusion

This report presents an example demonstrating the concept that adding metal nanoparticles into carbon may improve its lithium storage capacity without reducing the cycle life of the carbon as an electrode in a lithium-ion cell. The experimental cell was C(Pd)/0.5M LiI-50/50 (vol%) EC and DMC/Li, where C(Pd) was graphitized carbon fibers containing Pd nanoparticles. Whether the concept demonstrated in this report can be extended to the lithium-ion batteries that are practical for industrial applications is not known at this time. It will be investigated in further research.

Reference

[1] C. Hung, Extended Abstracts and Program, P.665, 22nd Biennial Conference on Carbon, July 16-21, 1995

Table 1: The capacity (mAh/g) of C(Pd) for lithium insertion/release during the entire experiment of 7 cycles

Cycle #	1	2	3	4	5	6	7
Voltage	0 – 2.5V			0 – 0.4V			
Insertion	399.1	283.9	277.8	276.1	239.9	237.7	236.7
Release	283.0	278.7	276.1	235.6	237.3	237.3	237.0

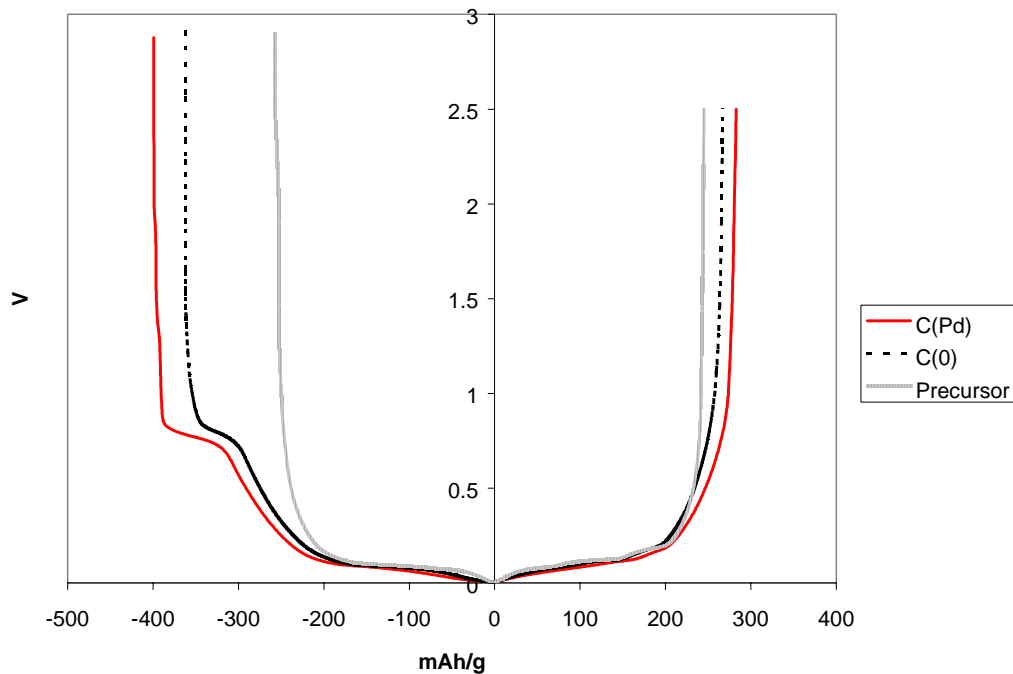


Figure 1: Voltages as functions of lithium storage capacity during the first cycle of lithium insetion/release.
 C(Pd): Carbon containing Pd nanoparticles; C(0): Pure carbon

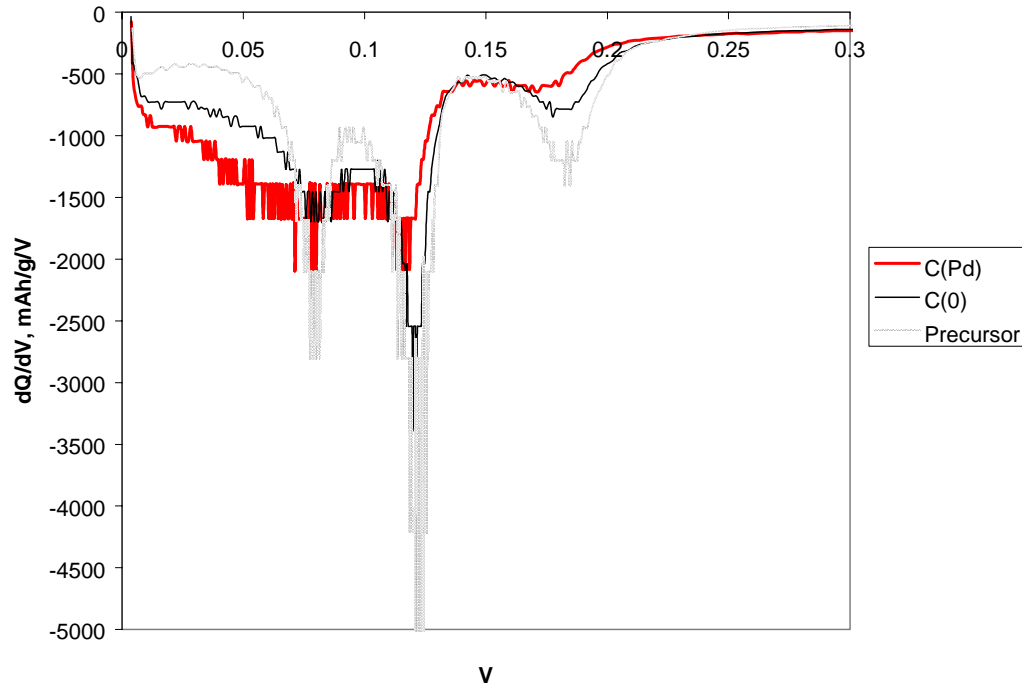


Figure 2: The rate of lithium release required to cause a unit of voltage change (dQ/dV_{wr}) as a function of voltage (V_{wr}).
 C(Pd): Carbon containing Pd nanoparticles; C(0): Pure carbon