

NASA/TM—2002-211312



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January 2002

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Prepared for the
Carbon Conference 2001
cosponsored by the ACS, Philip Morris, APMC, Westvaco,
Center for Applied Energy Research, Shunk, Calgon, Conoco,
Cfanshan, LexCarb, Procter & Gamble, Air Products,
Koppers Industries, and Quantachrome
Lexington, Kentucky, July 14–19, 2001

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This report contains preliminary findings, subject to revision as analysis proceeds.

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

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Summary

Carbon materials containing metal nanoparticles that can form an alloy with lithium were tested for their capacity and cycle life to store and release lithium electrochemically. Metal nanoparticles may provide the additional lithium storage capacity as well as additional channels to conduct lithium in carbon. The cycle life of this carbon-metal composite can be long because the solid-electrolyte interface (SEI) on the carbon surface may protect both lithium and the metal particles in the carbon interior. In addition, the voids in the carbon interior may accommodate the nanoparticle's volume change, and such volume change may not cause much internal stress due to small sizes of the nanoparticles. This concept of improving carbon's performance to store and release lithium was demonstrated using experimental cells of C(Pd)/0.5M LiI-50/50 (vol.%) EC and DMC/Li, where C(Pd) was graphitized carbon fibers containing palladium nanoparticles, EC was ethylene carbonate, and DMC was dimethyl carbonate. However, such improvement was not observed if the Pd nanoparticles are replaced by aluminum, possibly because the aluminum nanoparticles were oxidized in air during storage, resulting in an inert oxide of aluminum. Further studies are needed to use this concept for practical applications.

Introduction

Metals that can form an alloy with lithium may be used as anode in Lithium-ion batteries. Some of the metals have high lithium-storage capacity. For example, aluminum and tin have a theoretical capacity of 993 and 948 mAh/g, respectively [1]. However, anodes made from these metals generally had capacities far less than the above theoretical values, and their cycle lives were short. It is believed that the volume changes during lithium insertion-release and the resulting internal stress or disintegration are the reasons for their short cycle lives and low capacities. To counter such mechanical degradation, small active particles supported with less active or non-active matrices were proposed [2].

Carbon materials have been used for long life anodes. The long cycle life of carbon materials is a result of SEI (surface electrolyte interface) formation on the carbon surface during the first cycle of lithium insertion. The SEI prevents solvent from entering the carbon interior, and therefore prevents the formation of "dead regions" due to the reactions between solvents and lithium that is stored in the carbon interior during the later cycles [3].

The advantage of using carbon as a long cycle life anode in lithium-ion batteries is partially offset by the relatively low lithium storage capacity. Theoretically, in perfect graphite, a minimum of 6 carbon atoms are needed to accommodate one lithium, which translates into a theoretical maximum capacity of 372 mAh/g [4]. In certain non-graphite carbons, reversible lithium storage capacities higher than

the theoretical maximum for graphite have been made. For example, a commercial cell using hard carbon heat treated to presumably at around 1100 °C has the capacity of 400mAh/g [5].

It is proposed in this study that a carbon material containing metal nanoparticles that can form an alloy with lithium may have the advantages of both the metal and the carbon material. Metal particles provide the additional lithium storage capacity as well as additional channels to conduct lithium in carbon, and SEI on the carbon surface protects both lithium and the metal particles in the carbon interior. In addition, the effects of the nanoparticles volume changes during the lithium alloy formation may be minimized. This is because the voids in the carbon interior may accommodate the volume change, and may not cause much internal stress due to the small size of the particles.

This report studies and experimentally demonstrates the above-described concept.

Experimental

Carbon fibers containing palladium nanoparticles were fabricated by exposing fluorinated carbon fibers to a mixture of PdCl₂ and CuCl₂ in nitrogen environment at 310 to 370 °C, followed by heating in N₂ at 1100 °C. It is known that PdCl₂ alone does not react with fluorinated carbon, but a PdCl₂-CuCl₂ mixture does. Details of this fluorination-defluorination process were described previously [6–8].

The precursor of the carbon fibers was pitch-based Amoco P-100. The graphene layers were parallel to the fiber axes and perpendicular to the fiber surfaces. The majority of the atoms on the fiber surface were the carbon atoms at the edge of the basal plane.

Using mass analysis and energy dispersive spectroscopy (EDS) data, the composition of the fiber-nanoparticle composite 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}. The x-ray diffraction data indicated the presence of Pd and a small amount of PdCu₃. The size of the Pd particles was not measured. However, TEM data on similarly treated samples indicated most particles were in the 20 to 1000 Å range [7].

Carbon fibers containing aluminum nanoparticles were fabricated in a similar process [6,8], except AlCl₃ at 150 °C was used instead of the mixture of PdCl₂ and CuCl₂. The carbon mass % was estimated to be 92%. Other elements included aluminum and oxygen, where Al to O atomic ratio was about 2:1 (EDS data). However, the x-ray diffraction data indicated that the only non-carbon crystallites in this sample were gamma Al₂O₃.

Palladium and lithium can form a number of different alloys, LiPd_x, where x can range from 0.2 to 7. Aluminum and lithium form LiAl_y, where y can range from 2/3 to 3 [9,10]

For convenience, the above samples of carbon containing palladium or aluminum were labeled C(M), where M = Pd or Al. The carbon portion of this sample without the presence of the nanoparticles 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 [11]. This carbon material is labeled as C(0) in this report.

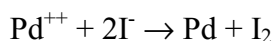
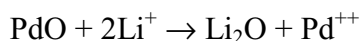
The fibers were tied to one end of a thin nickel string. The other end of the string was tied to a nickel rod, which was the electrode of a half cell, C(M)/0.5MLiI-50/50 (vol.%) EC and DMC/Li, using Li metal as the reference electrode. No binder was used for all electrodes used in this research.

Electrochemical tests were 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 0.4 V. The voltages difference between the working electrode and reference electrode (V_{wr}) was recorded once in every five minutes.

The same current (10 mA/g) was used to insert and release lithium to and from the carbon fibers that contained aluminum. Three cycles of lithium insertion-release were conducted between 0 to 2.5 V.

Results and Discussions

When placing the carbon fibers containing Pd nanoparticles into the electrolyte, the electrolyte at the proximity of the carbon turned purple. This phenomenon is believed to be the color of iodine resulting from the following reactions:



The sample described in this report had been stored in ambient air for about 1 year. It is believed that air reacted with the Pd nanoparticles in carbon slowly and steadily during this period. The x ray diffraction data did not show the presence of PdO, but the energy dispersive spectrum (EDS) data showed the presence of a small amount of oxygen. Further studies are needed to understand the effects of such oxygen on the performance of the carbon anode.

Figure 1 shows the voltage differences between the working electrode and reference electrode (V_{wr}) as functions of charge-discharge capacity (Q) during the first cycle of lithium insertion and release. Three samples, i.e., C(Pd), C(0), and their precursor, were used as the working electrodes. This figure indicates that the reversible 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(Pd) 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.

Sharp peaks for Pd-Li reaction did appear in a preliminary experiment. In this case the sharp peak in the dQ/dV_{wr} vs V_{wr} plot for lithium release reaction was observed at about 41.4mV. The carbon-palladium composite sample for this preliminary experiment was prepared differently. It was heated at 800 °C in nitrogen, stored in ambient air for a few days, and kept at a fully intercalated state for

50 hours between the lithium insertion and lithium release of the first cycle. This is compared to the C(Pd) sample described in Figures 1 and 2, which was exposed to 1000 °C heating in nitrogen, 1 year of ambient air storage, and less than one minute between the 1st lithium insertion and 1st lithium release.

There are two possible reasons to explain why some samples had a sharp Li-Pd reaction peak, but others did not. One of the reasons is that the presence of a small amount of oxygen in Pd nanoparticles prevent the formation of a homogeneous Li-Pd alloy. The other possible reason is that letting the working electrode at a fully intercalated state for 50 hours during the first cycle allowed enough time for the intercalated lithium to react to palladium nanoparticle, to form a homogeneous alloy, and therefore to have a constant dissociation voltage at 41.4 mV.

It is observed that if a homogeneous alloy is formed, it cannot be fully dissociated, resulting in a lower reversible capacity and a higher irreversible capacity. This preliminary sample had a reversible and irreversible capacities of 159 and 212 mAh/g, respectively. This can be compared to the irreversible and reversible capacity of C(Pd), which was 279 and 120 mAh/g, respectively.

Allowing the working electrode to remain at a fully intercalated state for 50 hours during the later cycles did not affect the samples' capacities or cycle life.

The rate of lithium release as a function of the voltage difference between working electrode and reference electrode (i.e., dQ/dV_{wr} vs V_{wr} plots) for this preliminary sample, the C(Pd) sample, and their precursor are described in Figure 3.

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 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 2.5 V range, the capacity of lithium insertion approached the capacity of lithium release. However, it appears that the capacity continued to decrease as more cycles of insertion and release were performed. A further examination of the V_{wr} -capacity curves for the 3 deintercalation half cycles (Figure 4) concluded that such decrease was the result of capacity loss at high voltage range ($0.4 \text{ V} < V_{wr} < 2.5 \text{ V}$). Because of this, the subsequent 4 cycles were performed in the 0 to 0.4 V range. After such an adjustment, the capacity loss disappeared. This suggests that the C(Pd) sample may have a long cycle life.

Figure 5 shows the voltages (V_{we}) of the C(Al), 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 reversible capacity for the C(Al) sample was smaller than that for either the same carbon without the presence of Al particles, C(0), or their precursor. From this figure and Figure 6 (dQ/dV_{wr} vs V_{wr} for lithium release reaction) it appears that Al was not an active element for reversible lithium storage. The aluminum atoms, however, may have contributed to the high value of the irreversible capacity (Table 2). It is possible that aluminum atoms that were partially reacted to oxygen became inert after receiving lithium during the first half cycle of the lithium insertion-release experiment.

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 consisted of C(Pd)/0.5M LiI-50/50 (vol.%) EC and DMC/Li, where C(Pd) was graphitized carbon fibers containing Pd nanoparticles. Such improvement was not observed if the Pd nanoparticles were replaced by aluminum, possibly because the aluminum nanoparticles were oxidized in air during storage, resulting in an inert oxide of aluminum. Whether the concept demonstrated in this report can be used to enhance the lithium-ion batteries that are used for industrial applications is not known at this time and will require further research.

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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

Table 2.—The capacity (mAh/g) of C(Al) for lithium insertion/release

Cycle #	1	2	3
Insertion	473	240	244
Release	206	208	212

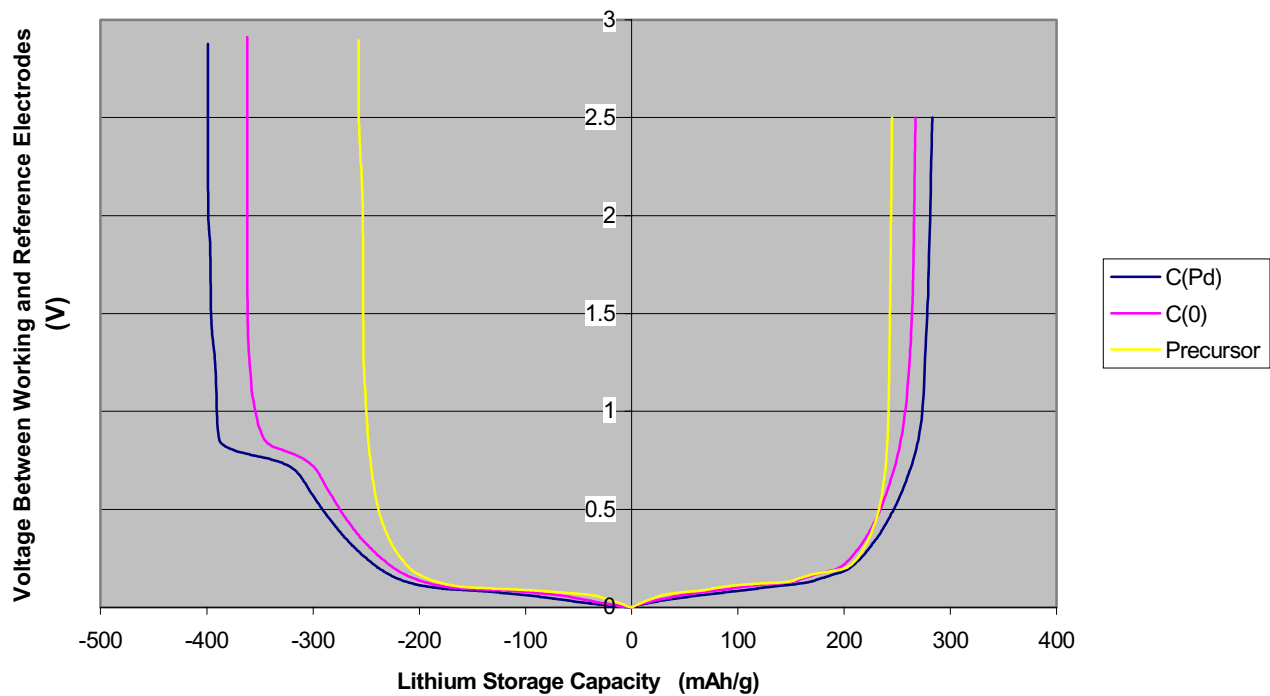


Figure 1.— Voltages as functions of lithium storage capacity during the first cycle of lithium insertion/release. C(Pd): Carbon containing palladium nanoparticles, C(0): Pure carbon without Pd nanoparticles, and their common precursor, P-100.

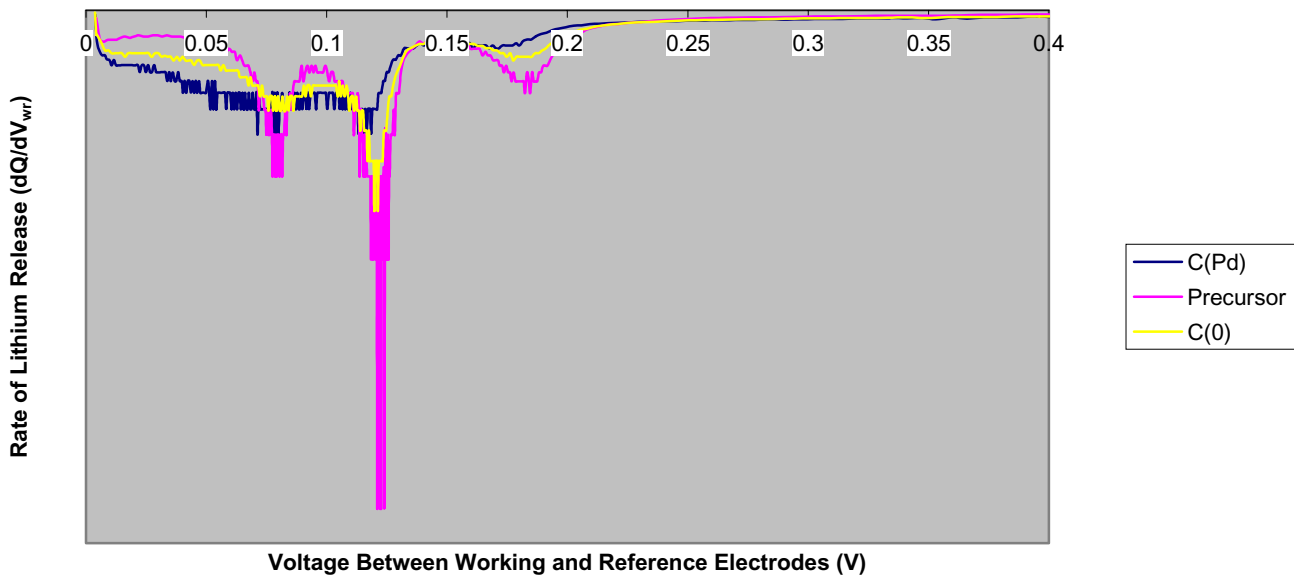


Figure 2.—Rates of lithium release (dQ/dV_{wr}) as functions of voltage (V_{wr}) for the following 3 samples: C(Pd): Carbon containing Pd nanoparticles, C(0): Pure carbon without Pd nanoparticles, and their common precursor, P-100.

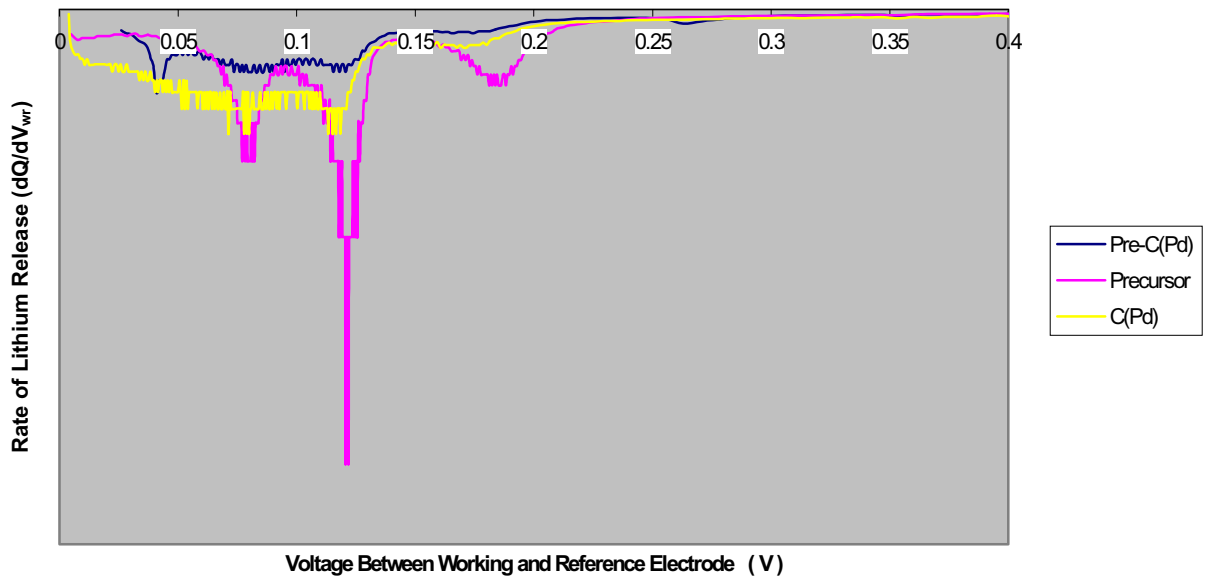


Figure 3.—Rates of lithium release (dQ/dV_{wr}) as functions of voltage (V_{wr}) for carbon-palladium nanoparticle samples having different duration of lithium saturation state between the end of lithium insertion and the beginning of the lithium release during the first cycle: Pre-C(Pd): Carbon-palladium nanoparticle composite with 50 hours of lithium saturation, C(Pd): Carbon-palladium nanoparticle composite with 80 seconds of lithium saturation. Precursors of both samples were pitch-based carbon fiber P-100.

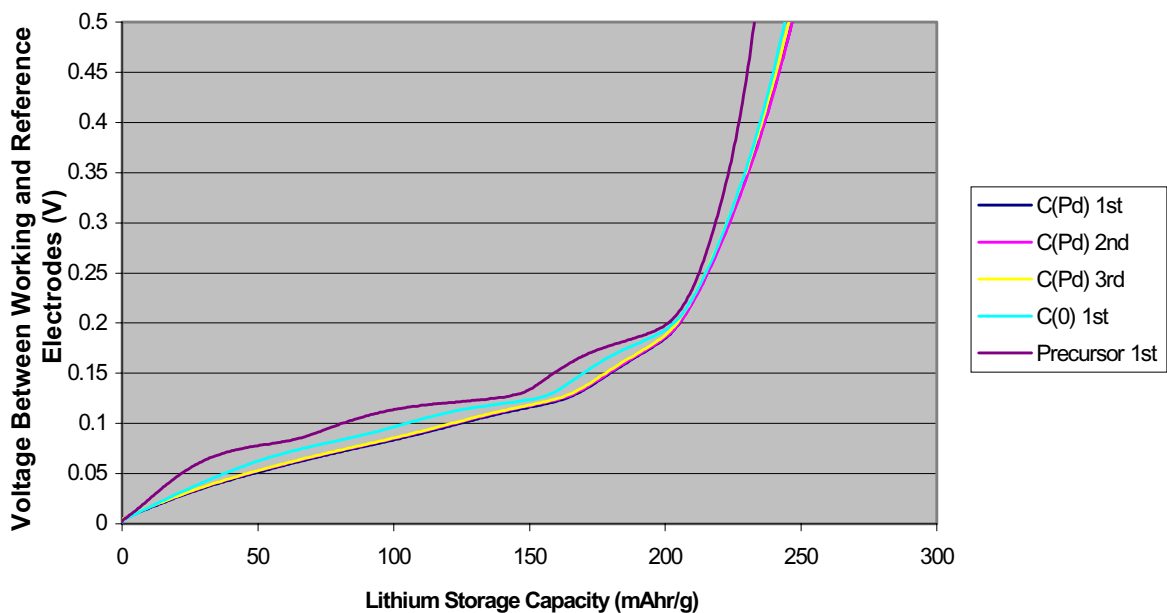


Figure 4.— Voltages as functions of lithium reversible capacity measured during lithium release in the first 3 cycles. C(Pd): Carbon containing Pd nanoparticles, C(0): Pure carbon without Pd nanoparticles, and their common precursor, P-100.

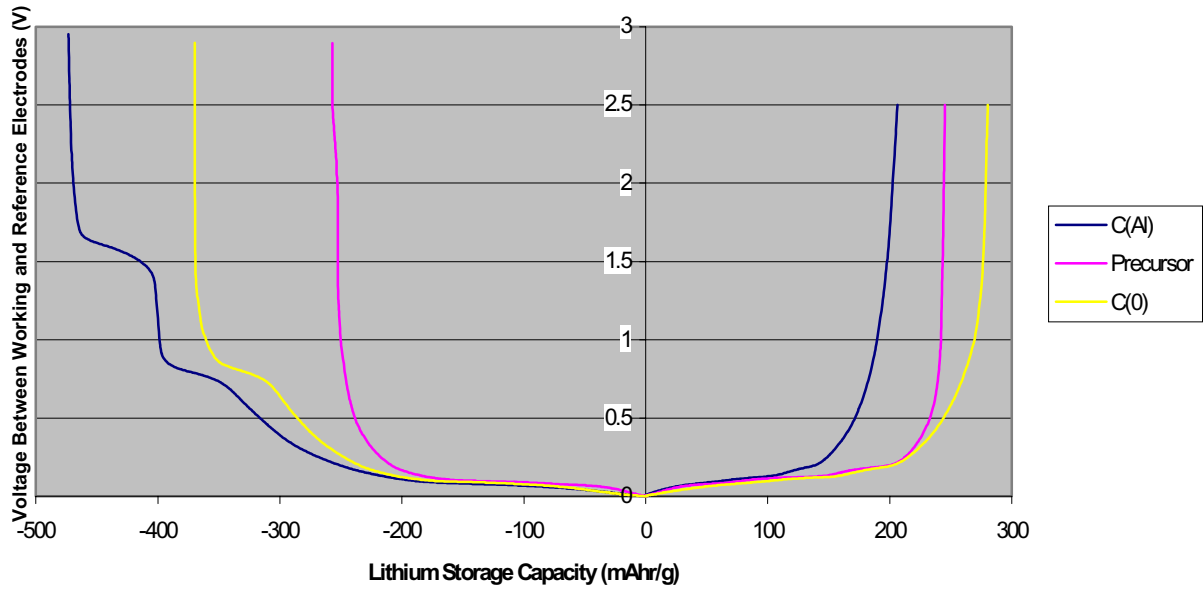


Figure 5.— Voltages as functions of lithium storage capacities during the first cycle of lithium insertion/release. C(Al): Carbon containing aluminum nanoparticles, C(0): Pure carbon without Al nanoparticles, and their common precursor, P-100.

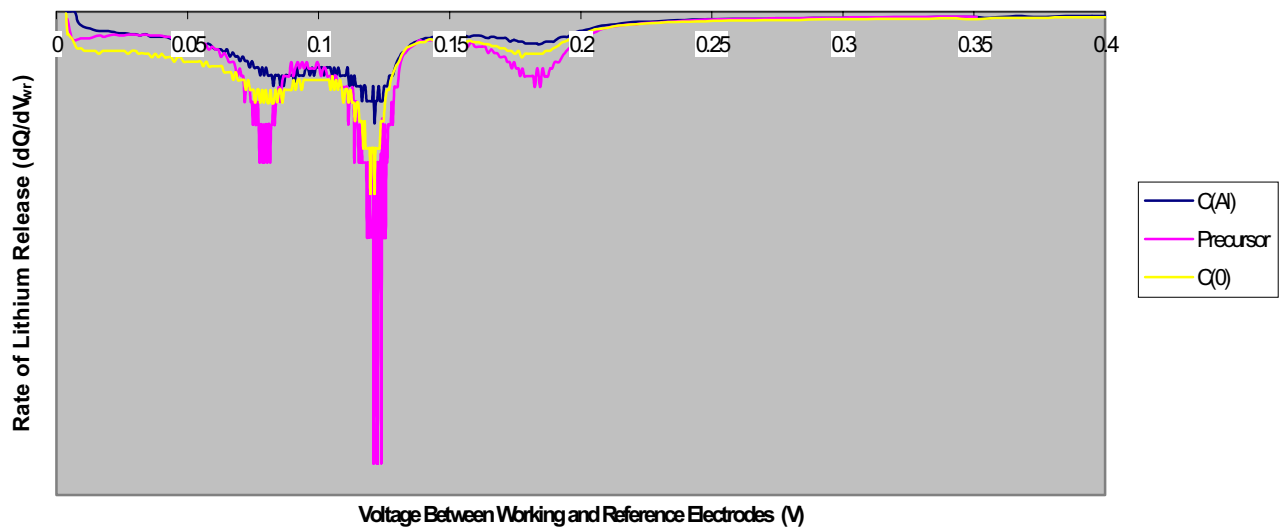


Figure 6.—Rates of lithium release (dQ/dV_{wr}) as functions of voltage (V_{wr}) for the following 3 samples: C(Al): Carbon containing aluminum nanoparticles, C(0): Pure carbon without aluminum nanoparticles, and their common precursor, P-100.

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE January 2002	3. REPORT TYPE AND DATES COVERED Technical Memorandum		
4. TITLE AND SUBTITLE Carbon Materials Embedded With Metal Nanoparticles as Anode in Lithium-Ion Batteries			5. FUNDING NUMBERS WU-755-1A-13-00	
6. AUTHOR(S) Ching-cheh Hung				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration John H. Glenn Research Center at Lewis Field Cleveland, Ohio 44135-3191			8. PERFORMING ORGANIZATION REPORT NUMBER E-13115	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration Washington, DC 20546-0001			10. SPONSORING/MONITORING AGENCY REPORT NUMBER NASA TM-2002-211312	
11. SUPPLEMENTARY NOTES Prepared for the Carbon Conference 2001 cosponsored by the ACS, Philip Morris, APMC, Westvaco, Center for Applied Energy Research, Shunk, Calgon, Conoco, Cfanshan, LexCarb, Procter & Gamble, Air Products, Koppers Industries, and Quantachrome, Lexington, Kentucky, July 14-19, 2001. Responsible person, Ching-cheh Hung, organization code 5480, 216-433-2302.				
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13. ABSTRACT (Maximum 200 words) Carbon materials containing metal nanoparticles that can form an alloy with lithium were tested for their capacity and cycle life to store and release lithium electrochemically. Metal nanoparticles may provide the additional lithium storage capacity as well as additional channels to conduct lithium in carbon. The cycle life of this carbon-metal composite can be long because the solid-electrolyte interface (SEI) on the carbon surface may protect both lithium and the metal particles in the carbon interior. In addition, the voids in the carbon interior may accommodate the nanoparticle's volume change, and such volume change may not cause much internal stress due to small sizes of the nanoparticles. This concept of improving carbon's performance to store and release lithium was demonstrated using experimental cells of C(Pd)/0.5M LiI-50/50 (vol.%) EC and DMC/Li, where C(Pd) was graphitized carbon fibers containing palladium nanoparticles, EC was ethylene carbonate, and DMC was dimethyl carbonate. However, such improvement was not observed if the Pd nanoparticles are replaced by aluminum, possibly because the aluminum nanoparticles were oxidized in air during storage, resulting in an inert oxide of aluminum. Further studies are needed to use this concept for practical applications.				
14. SUBJECT TERMS Lithium-ion battery; Nanoparticles; Lithium alloy			15. NUMBER OF PAGES 14	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT	