



UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY DOCKET NO	TOT CLAIMS	IND CLAIMS
61/500,560	06/23/2011		110	DENA-0008 (137124.00020)		

CONFIRMATION NO. 8442

25555
JACKSON WALKER LLP
901 MAIN STREET
SUITE 6000
DALLAS, TX 75202-3797

FILING RECEIPT



0C000000048595630

Date Mailed: 07/06/2011

Receipt is acknowledged of this provisional patent application. It will not be examined for patentability and will become abandoned not later than twelve months after its filing date. Any correspondence concerning the application must include the following identification information: the U.S. APPLICATION NUMBER, FILING DATE, NAME OF APPLICANT, and TITLE OF INVENTION. Fees transmitted by check or draft are subject to collection. Please verify the accuracy of the data presented on this receipt. **If an error is noted on this Filing Receipt, please submit a written request for a Filing Receipt Correction. Please provide a copy of this Filing Receipt with the changes noted thereon. If you received a "Notice to File Missing Parts" for this application, please submit any corrections to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections**

Applicant(s)

Clive P. Bosnyak, Dripping Springs, TX;
Kurt W. Swogger, Austin, TX;

Power of Attorney:

Amy Dunstan--61069

If Required, Foreign Filing License Granted: 07/05/2011

The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 61/500,560**

Projected Publication Date: None, application is not eligible for pre-grant publication

Non-Publication Request: No

Early Publication Request: No

**** SMALL ENTITY ****

Title

LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR
PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM

PROTECTING YOUR INVENTION OUTSIDE THE UNITED STATES

Since the rights granted by a U.S. patent extend only throughout the territory of the United States and have no effect in a foreign country, an inventor who wishes patent protection in another country must apply for a patent in a specific country or in regional patent offices. Applicants may wish to consider the filing of an international application under the Patent Cooperation Treaty (PCT). An international (PCT) application generally has the same effect as a regular national patent application in each PCT-member country. The PCT process **simplifies** the filing

page 1 of 3

of patent applications on the same invention in member countries, but **does not result** in a grant of "an international patent" and does not eliminate the need of applicants to file additional documents and fees in countries where patent protection is desired.

Almost every country has its own patent law, and a person desiring a patent in a particular country must make an application for patent in that country in accordance with its particular laws. Since the laws of many countries differ in various respects from the patent law of the United States, applicants are advised to seek guidance from specific foreign countries to ensure that patent rights are not lost prematurely.

Applicants also are advised that in the case of inventions made in the United States, the Director of the USPTO must issue a license before applicants can apply for a patent in a foreign country. The filing of a U.S. patent application serves as a request for a foreign filing license. The application's filing receipt contains further information and guidance as to the status of applicant's license for foreign filing.

Applicants may wish to consult the USPTO booklet, "General Information Concerning Patents" (specifically, the section entitled "Treaties and Foreign Patents") for more information on timeframes and deadlines for filing foreign patent applications. The guide is available either by contacting the USPTO Contact Center at 800-786-9199, or it can be viewed on the USPTO website at <http://www.uspto.gov/web/offices/pac/doc/general/index.html>.

For information on preventing theft of your intellectual property (patents, trademarks and copyrights), you may wish to consult the U.S. Government website, <http://www.stopfakes.gov>. Part of a Department of Commerce initiative, this website includes self-help "toolkits" giving innovators guidance on how to protect intellectual property in specific countries such as China, Korea and Mexico. For questions regarding patent enforcement issues, applicants may call the U.S. Government hotline at 1-866-999-HALT (1-866-999-4158).

LICENSE FOR FOREIGN FILING UNDER

Title 35, United States Code, Section 184

Title 37, Code of Federal Regulations, 5.11 & 5.15

GRANTED

The applicant has been granted a license under 35 U.S.C. 184, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" followed by a date appears on this form. Such licenses are issued in all applications where the conditions for issuance of a license have been met, regardless of whether or not a license may be required as set forth in 37 CFR 5.15. The scope and limitations of this license are set forth in 37 CFR 5.15(a) unless an earlier license has been issued under 37 CFR 5.15(b). The license is subject to revocation upon written notification. The date indicated is the effective date of the license, unless an earlier license of similar scope has been granted under 37 CFR 5.13 or 5.14.

This license is to be retained by the licensee and may be used at any time on or after the effective date thereof unless it is revoked. This license is automatically transferred to any related applications(s) filed under 37 CFR 1.53(d). This license is not retroactive.

The grant of a license does not in any way lessen the responsibility of a licensee for the security of the subject matter as imposed by any Government contract or the provisions of existing laws relating to espionage and the national security or the export of technical data. Licensees should apprise themselves of current regulations especially with respect to certain countries, of other agencies, particularly the Office of Defense Trade Controls, Department of

page 2 of 3

State (with respect to Arms, Munitions and Implements of War (22 CFR 121-128)); the Bureau of Industry and Security, Department of Commerce (15 CFR parts 730-774); the Office of Foreign Assets Control, Department of Treasury (31 CFR Parts 500+) and the Department of Energy.

NOT GRANTED

No license under 35 U.S.C. 184 has been granted at this time, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" DOES NOT appear on this form. Applicant may still petition for a license under 37 CFR 5.12, if a license is desired before the expiration of 6 months from the filing date of the application. If 6 months has lapsed from the filing date of this application and the licensee has not received any indication of a secrecy order under 35 U.S.C. 181, the licensee may foreign file the application pursuant to 37 CFR 5.15(b).

**IMPROVED LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES,
METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED
THEREFROM**

INVENTORS:

Clive P. Bosnyak
12001 Settlers Trail
Dripping Springs, Texas 78620 USA
Citizen of the United States

Kurt W. Swogger
4211 Waters Edge Cove
Austin, Texas, 78731, USA
Citizen of the United States

**IMPROVED LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES,
METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED
THEREFROM**

BACKGROUND

Lithium batteries are used extensively for portable electronic equipment and increasingly being used to provide electrical back-up for wind and solar energy. The commercially used Lithium ion (Li-ion) rechargeable batteries based on cobalt, nickel or manganese oxides for the cathode materials are known for their poor electrical conductivity and poor electrochemical stability which results in poor cycling (charge/discharge) ability. Olivine structures such as Lithium iron phosphate, LiFePO_4 or lithium manganese phosphate, LiMnPO_4 , operate at higher charge and discharge rates, but are still limited by low electrical conductivity and the kinetics of Li-ion diffusion.

Attempts to overcome the above deficiencies have included synthesis of nanocrystals of lithium salts as well as mixtures of lithium salts and carbon nanotubes. Even though the mixtures of carbon nanotubes and nanocrystals of lithium salts show improvements in charge/discharge rates the carbon nanotubes are not considered to be essentially discrete, i.e., individual tubes, nor attached to the tube. Also, the lithium nanocrystals are not ionically or covalently attached to the surface of the discrete carbon nanotubes to provide for intimate electron transfer and enhanced mechanical strength of the active material. Lithium salts have also been carbon coated to enhance electrical conductivity, but the carbon coating can slow the Lithium ion transport and may also react unfavorably with electrolytes over time.

In this invention we overcome the difficulties of low electrical conduction, improved lithium ion transport and mitigation of potentially damaging chemical side reactions by attaching nanosized crystals or nanosized layers of lithium ion active material to the surface of dispersed carbon nanotubes.

Likewise, for the lithium ion anode materials, active anode materials such as tin oxide or silicon can be attached to the discrete carbon nanotube surfaces to provide numerous benefits such as improved conductivity and mechanical strength.

In addition to the discrete carbon nanotube network providing support and spatial stabilization of nanosized particles or layers for cathode or anode material of the Lithium ion battery, other benefits include improved heat transfer media to avoid thermally-induced runaway, structural reinforcement to mitigate cracking of the active cathode or anode material due to expansion and contraction during charge and discharge cycles, and high surface area per weight of lithium ion active material to provide good energy density.

DETAILED DESCRIPTION

Experimental Examples

The following experimental examples are included to demonstrate particular aspects of the present disclosure. It should be appreciated by those of ordinary skill in the art that the methods described in the examples that follow merely represent illustrative embodiments of the disclosure. Those of ordinary skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments described and still obtain a like or similar result without departing from the spirit and scope of the present disclosure.

Example 1. Discrete Carbon Nanotubes with attached copper oxide nanoparticles suitable for a Lithium ion battery anode material.

102 mg of multi-wall carbon nanotubes oxidized to about 8 weight percent and aspect ratio about 60 are added to 100 mg copper sulfate, 640 mg sodium EDTA, 15 mg of polyethylene glycol, 568 mg of sodium sulfate and 60 mL of deionized water. The mixture is sonicated for 10 minutes and then heated to 40°C. 3 mL of formaldehyde (37% solution) and 500 mg of sodium hydroxide is added to bring the pH to 12.2. The mixture is stirred for 30 minutes at 85°C and then filtered using a 5 micron PVDF filter and washed with 200 mL of deionized water.

Example 2. Discrete Carbon Nanotubes with lithium iron phosphate coated on the surface of the tubes. suitable for a Lithium ion battery cathode material.

0.2 grams of multi-wall carbon nanotubes oxidized to about 8 weight percent and aspect ratio about 60 are added to 23.5 grams of diethylene glycol and sonicated for 15 minutes. The solution is grey. 1.16 grams of iron acetate dissolved in 4 ml of deionized water is added and the mixture

heated under nitrogen, stirring and sonication. After 1 hour at 140 degrees centigrade a solution of 0.65 grams of lithium acetate and 0.74 grams of ammonium phosphate in 4.2 ml of deionized water is added. The temperature is raised to about 185 degrees centigrade over 30 minutes then held at 185 degrees centigrade for 4 hours. The mixture is cooled to 110 C and sonicated for 5 minutes followed by further cooling to ambient temperature while stirring. The solids are separated from the mixture by centrifugation followed by ethanol washing. The resultant powder was dried in vacuo.

The resultant dried powder is determined to have a resistance of 2,000 ohm-cm compared to a commercially sample determined as 19,000 ohm-cm

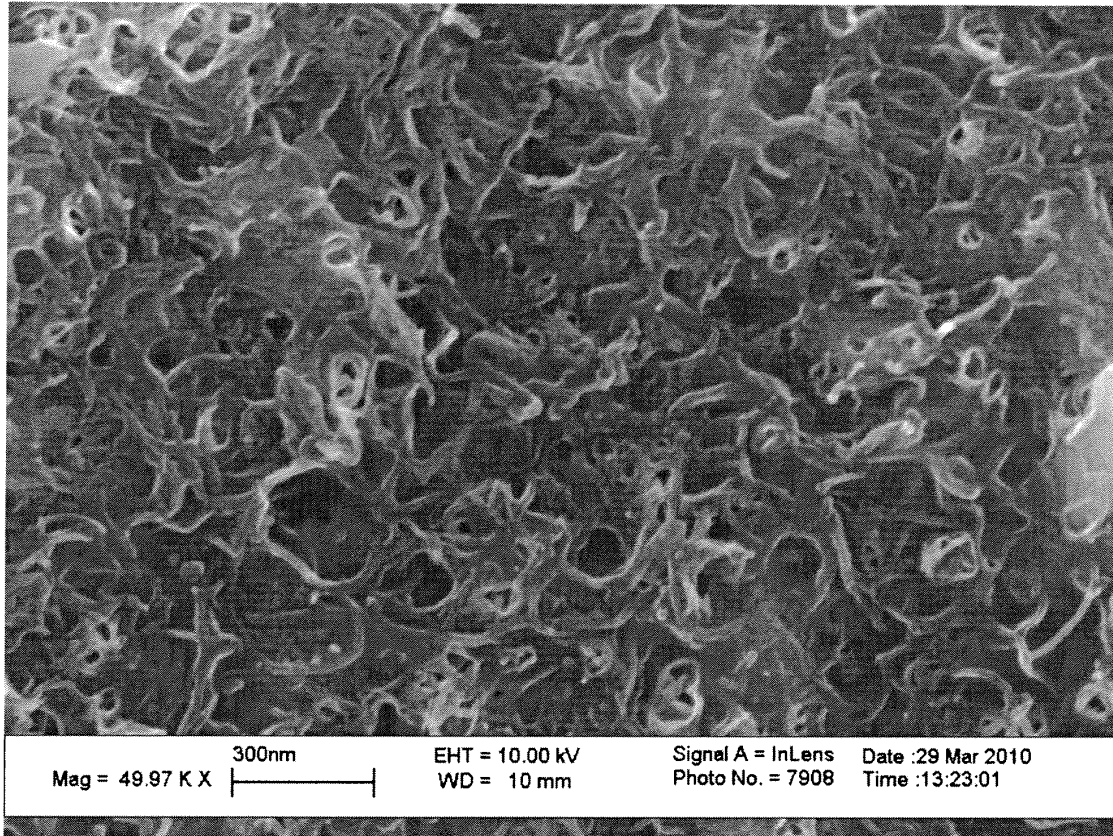
Example 3.

Lithium iron phosphate obtained commercially is ground with multiwall carbon nanotubes oxidized to about 8 weight percent and of aspect ratio about 60, in a mortar and pestle at weight ratios of 5:1 and 1:1 lithium salt to carbon nanotube. Sodium dodecyl sulfate SDS) is then added at a weight ratio of 0.7:1 compared to the carbon nanotube and deionized water added to resultant mixture to give a 0.5 weight percent solution of carbon nanotubes in the presence of lithium salt and surfactant. The mixture was sonicated for 1 hour, then the solids filtered using a PVDF filter (0.2 micron) washed with deionized water then dried. A micrograph of the discrete carbon nanotubes coated with lithium iron phosphate is shown in Figure 1. The results of the resistance of the powders is given in Table 1, units of resistance are ohm-cm.

Table 1

Material	5:1 Weight ratio Lithium salt:carbon nanotube	1:1 Weight ratio Lithium salt:carbon nanotube
Dry mix	860	26
Coated	46.2	6.9
Improvement of coating	18.6 X	3.8X

Figure 1. Lithium salt coated as a nanolayer on discrete carbon nanotubes.



CLAIMS

What is claimed is the following:

1. A composition useful for Lithium ion batteries comprising discrete carbon nanotubes having attached to their surface lithium ion active materials in the form of nanometer sized crystals or layers.
2. A composition of claim 1 wherein the lithium ion active material for a cathode comprises a lithium metal salt further comprising iron, manganese, cobalt, copper, nickel, vanadium, titanium, or mixtures thereof.
3. A composition of claim 2 further comprising the lithium metal salt with an olivine crystal structure.
4. A composition of claim 1 wherein the lithium ion active material for an anode comprises tin, silicon, copper, antimony, aluminum, Germanium or mixtures thereof.
5. A composition of claim 1 wherein the discrete carbon nanotubes have an aspect ratio of 25 to 500 and oxidation levels from 1 to 15% by weight of the carbon nanotube.
6. A composition of claim 1 further comprising graphene or oxygenated graphene.
7. A process for the production of the discrete carbon nanotubes having attached to their surface lithium ion active materials in the form of nanometer sized crystals or layers comprising the steps:
 - a) Selecting carbon nanotubes of aspect ratio 25 to 500 and oxidation level 1 to 15 weight percent.
 - b) Mixing the carbon nanotubes with a high boiling liquid, optionally with a non-ionic surfactant
 - c) Optionally sonicating the carbon nanotube liquid mixture
 - d) Adding reagents in correct balance to synthesize the desired lithium salt
 - e) Reacting the mixture at the desired temperature to form the lithium salt while sonicating the mixture
 - f) Separating the solid salts from the liquid.
 - g) Drying and annealing under an inert atmosphere the solid discrete carbon nanotubes with attached lithium salts at sufficient temperature to obtain the olivine crystal structure.
8. A process for the production of the discrete carbon nanotubes having attached to their

surface lithium ion active materials in the form of nanometer sized crystals or layers comprising the steps:

- h) Selecting carbon nanotubes of aspect ratio 25 to 500 and oxidation level 1 to 15 weight percent.
- i) Mixing the carbon nanotubes and desired lithium salt in a liquid with surfactant,
- j) Sonicating the carbon nanotube/lithium salt liquid mixture,
- k) Separating the solid salts from the liquid,
- l) Drying and annealing under an inert atmosphere the solid discrete carbon nanotubes with attached lithium salts at sufficient temperature to obtain the olivine crystal structure.

ABSTRACT

In various embodiments, exfoliated carbon nanotubes are described in the present disclosure. The carbon nanotubes maintain their exfoliated state, even when not dispersed in a medium such as a polymer or a liquid solution. Methods for making the exfoliated carbon nanotubes include suspending carbon nanotubes in a solution containing a nanocrystalline material, precipitating exfoliated carbon nanotubes from the solution and isolating the exfoliated carbon nanotubes. Nanocrystalline materials may include nanorods, hydroxyapatite and various hydroxyapatite derivatives. In some embodiments, methods for making exfoliated carbon nanotubes include preparing a solution of carbon nanotubes in an acid and filtering the solution through a filter to collect exfoliated carbon nanotubes on the filter. In some embodiments, a concentration of carbon nanotubes in the acid is below the percolation threshold. In other various embodiments, energy storage devices and polymer composites containing exfoliated carbon nanotubes are described herein. The energy storage device may be a battery containing at least two electrodes and an electrolyte in contact with the at least two electrodes. At least one of the electrodes in the energy storage device advantageously contains exfoliated carbon nanotubes. The polymer composites are prepared by mixing exfoliated carbon nanotubes with a polymer material. After being mixed in the polymer material, the carbon nanotubes maintain their exfoliated state.

Doc Code: **TR.PROV**

Document Description: Provisional Cover Sheet (SB16)

PTO/SB/16 (11-08)

Approved for use through 09/30/2010 OMB 0651-0032

U.S. Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number

Provisional Application for Patent Cover Sheet					
This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c)					
Inventor(s)					
Inventor 1					Remove
Given Name	Middle Name	Family Name	City	State	Country
Clive	P.	Bosnyak	Dripping Springs	TX	US
Inventor 2					Remove
Given Name	Middle Name	Family Name	City	State	Country
Kurt	W.	Swogger	Austin	TX	UA
All Inventors Must Be Listed – Additional Inventor Information blocks may be generated within this form by selecting the Add button.					Add
Title of Invention		IMPROVED LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS...			
Attorney Docket Number (if applicable)		DENA-0008 (137124.00020)			
Correspondence Address					
Direct all correspondence to (select one):					
☒ The address corresponding to Customer Number			☐ Firm or Individual Name		
Customer Number			25555		

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.	
☒ No.	
☐ Yes, the name of the U.S. Government agency and the Government contract number are:	

Entity Status					
Applicant claims small entity status under 37 CFR 1.27					
☒ Yes, applicant qualifies for small entity status under 37 CFR 1.27 ☐ No					
Warning					
Petitioner/applicant is cautioned to avoid submitting personal information in documents filed in a patent application that may contribute to identity theft. Personal information such as social security numbers, bank account numbers, or credit card numbers (other than a check or credit card authorization form PTO-2038 submitted for payment purposes) is never required by the USPTO to support a petition or an application. If this type of personal information is included in documents submitted to the USPTO, petitioners/applicants should consider redacting such personal information from the documents before submitting them to USPTO. Petitioner/applicant is advised that the record of a patent application is available to the public after publication of the application (unless a non-publication request in compliance with 37 CFR 1.213(a) is made in the application) or issuance of a patent. Furthermore, the record from an abandoned application may also be available to the public if the application is referenced in a published application or an issued patent (see 37 CFR 1.14). Checks and credit card authorization forms PTO-2038 submitted for payment purposes are not retained in the application file and therefore are not publicly available.					
Signature					
Please see 37 CFR 1.4(d) for the form of the signature.					
Signature	//Amy U. Dunstan//			Date (YYYY-MM-DD)	2011-06-23
First Name	Amy U.	Last Name	Dunstan	Registration Number (If appropriate)	61069
This collection of information is required by 37 CFR 1.51. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. This form can only be used when in conjunction with EFS-Web. If this form is mailed to the USPTO, it may cause delays in handling the provisional application.					

Electronic Patent Application Fee Transmittal				
Application Number:				
Filing Date:				
Title of Invention:		IMPROVED LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM		
First Named Inventor/Applicant Name:		Clive P. Bosnyak		
Filer:		Amy L. Ulfers/Debbie Sams		
Attorney Docket Number:		DENA-0008 (137124.00020)		
Filed as Small Entity				
Provisional Filing Fees				
Description	Fee Code	Quantity	Amount	Sub-Total in USD(\$)
Basic Filing:				
Provisional Application filing fee	2005	1	110	110
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD(\$)
Miscellaneous:				
Total in USD (\$)				110

Electronic Acknowledgement Receipt	
EFS ID:	10376992
Application Number:	61500560
International Application Number:	
Confirmation Number:	8442
Title of Invention:	IMPROVED LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM
First Named Inventor/Applicant Name:	Clive P. Bosnyak
Customer Number:	25555
Filer:	Amy L. Ulfers/Debbie Sams
Filer Authorized By:	Amy L. Ulfers
Attorney Docket Number:	DENA-0008 (137124.00020)
Receipt Date:	23-JUN-2011
Filing Date:	
Time Stamp:	19:28:35
Application Type:	Provisional

Payment information:

Submitted with Payment	yes
Payment Type	Deposit Account
Payment was successfully received in RAM	\$ 110
RAM confirmation Number	7746
Deposit Account	100096
Authorized User	

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
-----------------	----------------------	-----------	----------------------------------	------------------	------------------

1	Specification	DENA_08_Specification.pdf	1001875 3692fed8d9c41b343ebb6b7c76f6f877152c bcd8	no	5
Warnings:					
Information:					
2	Claims	DENA_08_Claims.pdf	94373 7f6314d3cf10a4ce38be9f6c916fea3839ebe 29e	no	2
Warnings:					
Information:					
3	Abstract	DENA_08_Abstract.pdf	54862 5daea6de1db345885779a22e7e108bef2de bd521	no	1
Warnings:					
Information:					
4	Provisional Cover Sheet (SB16)	PRO_Cover_Sheet.pdf	28841 4bd871c7c3c242b84f43b841c3095141c27 b8ab7	no	2
Warnings:					
This is not a USPTO supplied Provisional Cover Sheet SB16 form.					
Information:					
5	Fee Worksheet (SB06)	fee-info.pdf	29935 c0ed8998afc944ddb72daf3cb80ce8ddcc 3e419	no	2
Warnings:					
Information:					
Total Files Size (in bytes):			1209886		
This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.					
<u>New Applications Under 35 U.S.C. 111</u> If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.					
<u>National Stage of an International Application under 35 U.S.C. 371</u> If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.					
<u>New International Application Filed with the USPTO as a Receiving Office</u> If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.					