

Novel materials for electrochemical power sources—introduction of PUREBLACK® Carbons

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Abstract

Graphitization heat treatment of a precursor carbon black was seen to effectively produce a wide variety of forms of partially graphitized nano-sized carbonaceous materials with a set of unique properties, some of which are reported in this paper in comparison with those properties of the precursor carbon material. These novel materials were given the name of PUREBLACK® Carbons.

Among some of the unique properties are: higher conductivity than that of acetylene type carbon blacks due to PUREBLACK® Carbon's particles having more graphitic structure; very low to zero volatile content (external oxygen, sulfur, etc., groups, which are often believed to be the cause of initiation of self-discharge reactions in batteries); very low equilibrium moisture pickup (20 ppm level), which makes it particularly attractive in lithium metal or lithium-ion based electrochemical systems; high purity. Electrochemical testing of the newly proposed PUREBLACK® Carbons in several battery systems offers significant promise that it presents a viable solution to the needs of industry.

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1. Introduction

The size of the worldwide battery industry in terms of its production volume is estimated at over 40 billion bat-

teries/cells per year [1]. Currently, there are over 30 commercially viable battery chemistries and practically each type of battery uses some form of carbonaceous material in its composition [2]. It is estimated that the industry of power sources requires in excess of 50,000 tonnes of various carbonaceous materials [3], and some sources predict that consumption of certain types of graphitic carbon by this industry may double in the next five to seven years [4].

For decades, the industry of power sources (in our definition, it includes batteries, fuel cells and electrochemical supercapacitors) has been focusing on the use of mainly two types of carbon: synthetic graphite and acetylene type carbon black [5].

However, in recent years, a number of significant improvements in the various battery technologies were associated with introduction of new, advanced forms of carbonaceous materials, which currently keep on successfully replacing two traditional types of carbon mentioned above. These novel types of carbon include: purified natural [6,7], thermally exfoliated [8], engineered [9], increased density surface-treated graphite and carbons [10,11], available from Superior

Abbreviations: AIMS, Superior Graphite's acronym for Adaptive Integrated Management System; DMC, dimethyl carbonate, an organic electrolyte solvent for lithium-ion batteries; DME, 1,2-dimethoxyethane, an organic electrolyte solvent for lithium primary batteries; EC, ethylene carbonate, an organic electrolyte solvent for lithium-ion batteries; EMD, electrolytic manganese dioxide, MnO₂; IUPAC, International Union of Pure and Applied Chemistry, an international standards organization; Li/MnO₂, lithium/manganese dioxide primary cell (battery); Li/SOCl₂, lithium/thionyl chloride primary battery; NMP, *n*-methyl pyrrolidone, a solvent used to process PVDF binders; o.c.v., open circuit voltage; PC, propylene carbonate, an organic electrolyte solvent for lithium primary and lithium-ion batteries; PEM fuel cell, polymer electrolyte membrane type of fuel cells; PTFE, polytetrafluoroethylene, an organic binder for cathodes of lithium primary cells; PUREBLACK® Carbons, graphitized carbon blacks, a product line jointly developed and being commercialized by Superior Graphite (Chicago, IL, USA) and Columbian Chemicals Co. (Marietta, GA, USA); PVDF, polyvinylidene fluoride, a copolymer binder used in lithium-ion battery technologies

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Graphite, a leading industrial carbons supplier to the industry of power sources [12].

The purpose of this paper is to introduce a newly developed form of the nano-sized graphitic carbon, which is expected to offer a viable alternative to the acetylene type carbon black, and be applicable to most electrochemical applications.

2. Experimental/materials and methods

In this paper, we used a variety of analytical data obtained on the equipment and with the techniques established at the Peter R. Carney Technology Center of Superior Graphite (Chicago, IL, USA) and at the Research and Development Center of Columbian Chemicals Co. (Marietta, GA, USA). Description below outlines main methods and equipment used in this work.

2.1. Physicochemical characterization

The amount of volatile matter in the carbonaceous materials under investigation has been determined using Superior Graphite's standardized Adaptive Integrated Management System (AIMS)/ISO9001:2000 quality procedure known as "volatile content". In accordance with this procedure, a dried sample of carbon material undergoes controlled oxidation and pyrolysis in a special covered crucible at 925 ± 10 °C for 7 min. After cooling sample in air, the percentage by weight loss is calculated.

The amount of sulfur impurities in the carbonaceous materials discussed in this paper has been detected using Superior Graphite's standardized AIMS/ISO9001:2000 quality procedure known as "Sulfur". In LECO Corp.'s SC-144DR Sulfur/Carbon Determinator module, a sample of carbon material undergoes combustion at elevated temperatures in an oxygen rich atmosphere. The sulfur dioxide content of the combustion gases is measured and used to determine percent or ppm sulfur.

Two methods were used to determine moisture in the carbon materials discussed in this paper.

For moisture levels in excess of 0.1 wt% (1000 ppm), a Superior Graphite's standardized AIMS/ISO9001:2000 quality technique called "Free Moisture Content of Carbon Materials" was used. In accordance with this procedure, a 2 g carbon sample is heated at 110 ± 10 °C for 2 h. Precautions are taken in sample handling to prevent loss or gain of atmospheric moisture. The percentage by weight loss is calculated. This method becomes inaccurate once moisture levels of below 0.05 wt% (500 ppm) need to be determined. Such low moisture is often referred to as "bound moisture of carbon materials". The bound moisture has been assessed by Karl Fischer moisture titration (instruments used were: model Metrohm 756 KF Coulometer with 707 KF oven, available from Brinkmann Instruments, Inc. of Westbury, NY, USA).

In the Karl Fischer method, a 1 g sample is placed in a pre-dried boat and introduced to an oven, where the temperature is set and maintained at 280 °C. The carbon material

sits in the oven for 10 min. During this time, the moisture driven off the carbon structure is carried into a coulometric vessel by a stream of air or nitrogen (optional). This vessel determines moisture content by utilizing a methonic solution of iodine, sulfur dioxide and a base as buffer. Since I_2 reacts quantitatively with H_2O , this instrument uses this reaction to form the basis of water determination.

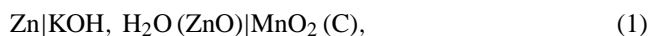
The ash fraction (i.e. the mineral impurities) in the carbon materials studied in this work has been broken down into individual elements and their specific concentrations, as measured in ppm or ppb levels, were determined with an ICP inductively coupled plasma spectrometer (Model Jobin Yvon Ultima POXX/681, available from Horiba Group, Longjumeau, France) after leaching impurities out from carbons in a mixture of nitric and sulfuric concentrated acids.

The equilibrium moisture pickup referred to in this paper has been determined by author's colleagues and partners on subject new development, Columbian Chemicals Co. The procedure used to carry out the measurements was as follows. The carbon sample is dried under vacuum (1 mmHg or less) at 100 ± 10 °C for at least 4 h. The sample is removed from the vacuum system while still under vacuum and transferred to a glove box at controlled temperature and humidity (humidity of $71 \pm 3\%$ and temperature of 23 ± 2 °C were maintained). The vacuum is removed and the sample of a carbonaceous material is immediately transferred to a pre-weighed aluminum dish and the weight of a carbon sample is determined. After that, the sample is weighed at regular intervals (every 15 min for first 1 h, then every 4 h for next 24 h and then every 24 h) in order to determine the moisture pickup. Using the above procedure, the equilibrium moisture pickup was measured over a period of one week.

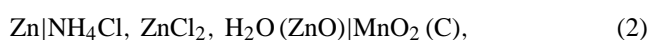
Characterization of the nano-sized carbon particles discussed throughout this paper has been performed using transmission electron microscope (TEM) imaging. As far as preparation of the carbon samples and doing the TEM analysis are concerned, these methods are explicitly described elsewhere (see, for instance, [13]). The high resolution TEM imaging used in this work is a courtesy of Columbian Chemical Co.

2.2. Electrochemical characterization

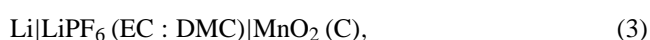
In order to highlight capabilities of the newly developed carbon materials proposed in this work, authors have attempted to characterize their performance in three electrochemical systems, as follows:



often referred to as alkaline-manganese dioxide primary cells, or alkaline batteries;



known as zinc chloride cell system or zinc-carbon battery;



a variation of lithium/manganese dioxide (Li/MnO₂) primary battery with more advanced electrolyte system than what is being typically used for this chemistry (LiClO₄ in propylene carbonate (PC)/1,2-dimethoxyethane (DME)).

The electrochemical cells of standard sizes, as described below, were manufactured and tested at Superior Graphite's Peter R. Carney Technology Center. Where applicable, the electrochemical performance of these cells was compared with the behavior of commercially available cells, purchased in retail stores in greater Chicago, IL, USA, in the timeframe of testing internally manufactured cells.

2.2.1. Description of the alkaline-manganese dioxide primary cell used in this work

The typical electrochemical device used for testing of behavior of the carbon materials in the alkaline-manganese dioxide primary cell (Eq. (1)) was a coin cell of a standard LR2016 size (20 mm in diameter and 1.6 mm high). The construction of such cells can be referenced to the published literature [2], but we describe it herein such that logic behind our results can be understood.

A coin cell battery consists of the following main components. Stainless steel anode cup, cathode cup and a nylon gasket represent a housing of the battery. The interior of the cathode cup is airbrushed with graphite-containing can coating. Such coating, for instance, is available from Superior Graphite and is called FormulaBT CC9005. The cathode consists of the active material electrolytic manganese dioxide (EMD, MnO₂). An example of such material is AB—standard alkaline battery grade available from Kerr McGee, a USA company. For the electrochemical data reported in this paper, the amount of EMD in the cathodes was approximately 0.35 g. The amount of carbon with EMD will depend on the purpose of the test. Herein, in order to show ability of novel carbons to work as efficient conductivity enhancement additives at low loadings, we reported data for EMD/carbon ratios of 20/1. The wet cathode mix (impregnated with electrolyte based on 37 wt% KOH) is pressed into the pre-coated with a can coating and dried cathode cup. The pressure is applied by a semi-automatic hydraulic press, which is available from Carver, Inc., a USA manufacturer. The pressure amounting to approximately 3000 kg cm⁻² is applied during 30 s to form a cathode pellet. The final electrode thickness is monitored and controlled as a measure of density of the electrode. Two layers of the non-woven separator were used to separate cathode from the anode. The anode is based on a zinc powder, available from Doral Distributions, a Swiss company (grade: Zinc Doralloy 104 (particle size below 0.036 mm)). Its amount is balanced to be equal in molar ratio to the amount of EMD in the counter electrode. The anode paste as well is impregnated with KOH-based electrolyte prior to assembling of the cell. The battery is sealed by the means of a crimping device available for this type of cells from Hoshen Corp. of Japan.

2.2.2. Description of the zinc chloride primary cell used in this investigation

The typical electrochemical device used for testing of behavior of the carbon materials in the zinc chloride primary cell (Eq. (2)) was a cylindrical AA (R6) standard size cell (approximately 14 mm in diameter and 50 mm high). The construction of such cells is in principle, state-of-the-art knowledge, and can be referenced to the battery textbook [2]. However, Superior Graphite's laboratory-designed cells have a unique design, and therefore, we describe it herein, also for the reason of explaining the logic behind our experiments.

Zinc can together with top metal cover and a layer of sealant form the exterior of cells. The interior of the cell is comprised of a paste separator attached to zinc can from the inside; a cathode, which is approximately 38 mm high (out of 50 mm of the total height of the cell); a carbon rod, which serves as cathode's current collector and a gas vent at the same time; a gas chamber, which is approximately 4 mm high; and a set of separating and structural support washers, which prevent short circuits inside the cell. A departure from traditional cylindrical battery designs is application of minute quantities of sealant (glue for plastics) instead of asphalt seals, which are difficult to process and they take up too much space in a battery, thus decreasing its volumetric energy density.

The interior of the cell contains zinc chloride-based electrolyte. Although there is a world of electrolyte compositions for zinc chloride cells, the data reported here in are based on 40 wt% ZnCl₂, 0.5 wt% NH₄Cl and 0.25 wt% ZnO.

The agglomerate of the positive active mass is prepared separately before forming it into the cathode. For results discussed in this work, the active mass consisted of MnO₂ with 8 wt% of carbon material (type of carbon material used was the key variable in our experiments). An electrolyte is added into the cathodic mass after a thorough dry mixing of MnO₂ and carbon is complete. The amount of electrolyte absorbed by the agglomerate is noted. In the next stage, the agglomerate is funneled into the zinc can, which already has an electrolyte-impregnated separator attached to its interior wall. The funnel has a unique shape, which allows insertion of a carbon rod current collector after mechanical formation of the cathode.

After placement of separating washers, forming the internal gas chamber, sealing tight gaps with a sealant, the cell is crimped and checked for short circuit current and open circuit voltage (o.c.v.) with a milliohmmeter (model: Fluke, a USA product). The cell is held for a minimum of 10 h before discharging it on a battery cycler. Storage of the cell results in uniform distribution of electrolyte within the electrochemical device and ensures very repeatable performance from cell to cell.

2.2.3. Description of lithium/manganese dioxide primary cell used in this study

The electrochemical device used for testing of behavior of the carbon materials in the lithium/manganese dioxide primary cell (Eq. (3)) was a coin cell of a standard CR2325 size (23 mm in diameter and 2.5 mm high). We would like

to reference readers to the published literature [2], where the cutaway viewgraphs showing construction of such coin cells can be found.

The exterior of CR2325 is made up of a stainless steel anode cup, cathode cup and a polypropylene gasket. The interior of the cathode cup contains a thin nickel mesh, spot-welded to the stainless steel substrate in order to enhance adhesion of the cathode to the current collector.

A classic Li/MnO₂ cell uses lithium foil for the anode, and electrolyte containing lithium salts in a mixed organic solvent (LiClO₄ in PC/DME). For the cathode, it uses a specially prepared heat-treated form of MnO₂ (active material) mixed with 8–12 wt% carbon/graphite and up to 4 wt% polytetrafluoroethylene (PTFE) binder.

The electrochemical cells made for this work had few improvements over traditional Li/MnO₂ systems, with the major one being a different electrolyte system. We used an electrolyte from the lithium-ion battery systems (i.e. ethylene carbonate (EC):dimethyl carbonate (DMC) (1:1), LiPF₆ (1 M) made by Cheil Industries, Samsung Group, South Korea). We believe, substitution of electrolyte had a role in improvement of the overall battery performance, but since the chief purpose of our experiments was comparison of Li/MnO₂ battery performance as function of carbon type used in the cathode, presence of a different electrolyte should not be viewed as a critical departure from performance to be expected in traditional battery chemistry.

Preparation of cathode goes through a step of heat treatment of MnO₂. The starting material used in our tests was the EMD form of MnO₂ (the AB—alkaline battery grade available from Kerr McGee, a USA company). Any temperature above 110 °C and even 110 °C for times greater than approximately 2 h will damage the EMD. It loses some of its structural water and the structural changes associated with this are detrimental for EMD. The process seems to be irreversible, and per Swinkels [14], the reason is that EMD is a non-equilibrium structure. On heating, it changes to a more equilibrium state (towards pyrolusite). Such heat treatment is believed to result in conversion of EMD (gamma-crystalline structure of MnO₂) to beta-manganese dioxide, a crystalline structure preferred in the Li/MnO₂ cells.

There are a variety of ways how to convert EMD into the beta-MnO₂ phase. For instance, a Duracell patent [15] teaches to producing beta-manganese dioxide in a rotary tube furnace through a continuous (0.045–1.36 kg min⁻¹) process of heating gamma-manganese dioxide at at least 450 °C for up to 1 h (after pre-heating the mix at up to 300 °C) in order to convert a majority (60–90% conversion) of the gamma-manganese dioxide to the beta-phase without forming detrimental amounts of lower oxides.

In our work, the conversion of EMD to the beta-MnO₂ was carried out in a tube furnace under a constant flow of nitrogen, at a temperature of 300 °C for 3 h. The resultant product was mixed with 5–8 wt% of carbon material (variable of this investigation depending on carbon type). Instead of approximately 4 wt% of PTFE (typically used in

Li/MnO₂ technology), we added 1 wt% polyvinylidene fluoride (PVDF) binder into the cathode composition (it comes as *n*-methyl pyrrolidone (NMP)-pre-dissolved PVDF solution, grade KF#9305, available from Kureha Advanced Materials Division, Tokyo, Japan). The cathode mass was dried and pressed into the cathode cup, and then again dried under vacuum at 120 °C. Cells were assembled in the argon-filled glove box where concentration of H₂O was kept at below 1 ppm (UniLab system available from MBraun, Inc. of Stratham, NH, USA). Cells were hermetically sealed by the way of crimping before testing.

2.2.4. Electrochemical testing

In order to make conclusive statements, the authors manufactured up to 20 cells of each formula. Cells were discharged using a multi-channel battery cycler (model BT2000 Basic Charge, available from Arbin Instruments of College Station, TX, USA). The current densities applied to the cells are test-specific and are described in detail in Section 4.

3. Theory

Initially, the creation of the novel nano-sized graphitic family of carbon materials, PUREBLACK[®] Carbons, had been done in response to a trend taken by many battery technologies, that is the reduction of the particle size of active materials, which often leads to the higher power density characteristics of the batteries. Carbon, being usually used as electrically conductive additive (as part of the blend with the active material), needs to go finer in size as active materials become finer. At some point of time (after about 1–3 μm), it is no longer efficient to reduce starting carbon's size through grinding/classification, and rather, starting with a different precursor can be contemplated. We have proposed that such new precursor might be, for instance, various forms of carbon black.

Per definition of International Union of Pure and Applied Chemistry (IUPAC), carbon black is an industrially manufactured colloidal carbon material in the form of spheres and of their fused aggregates with sizes below 1000 nm (1 μm). Carbon black is a commercial product manufactured by thermal decomposition of hydrocarbons, including detonation, or by incomplete combustion of carbon hydrogen compounds and has a well-defined morphology with a minimum content of tars or other extraneous materials [16].

In reality, there are a great variety of forms of carbon black. Grades of carbon black differ by their particle size, particle shape and a number of other properties, depending on specific application they are intended for. Columbian Chemicals Co., one of the world's largest commercial producers of nano-structured carbon materials, produces various forms of carbon black, which we used as precursors in this work. This company carries over 300 standard carbon black products, and the 2 extreme examples, which we considered in our

joint studies, became high structure, 30–70 nm sized, acetylene type carbon blacks and spherical, stand-alone particles of thermal black, which come in particle sizes in the range of approximately 300–500 nm.

It has been contemplated that heat treatment of these precursors at graphitizing temperatures (in excess of 2000 °C) might produce a wide variety of forms of partially graphitized nano-sized carbonaceous materials of new type that would feature a set of unique properties. This theory became a foundation of the further work that authors are reporting in Section 4.

4. Results and discussion

4.1. PUREBLACK[®] Carbon—a new form of nano-sized carbonaceous material is born

We would like to draw reader's attention to the typical TEM images of ungraphitized precursor used in this work, i.e. carbon black, as shown in Fig. 1(a). Fig. 1(b) shows, for reference, a TEM image of acetylene black, a material widely used in battery applications, mainly for conductivity enhancement and electrolyte absorption purposes.

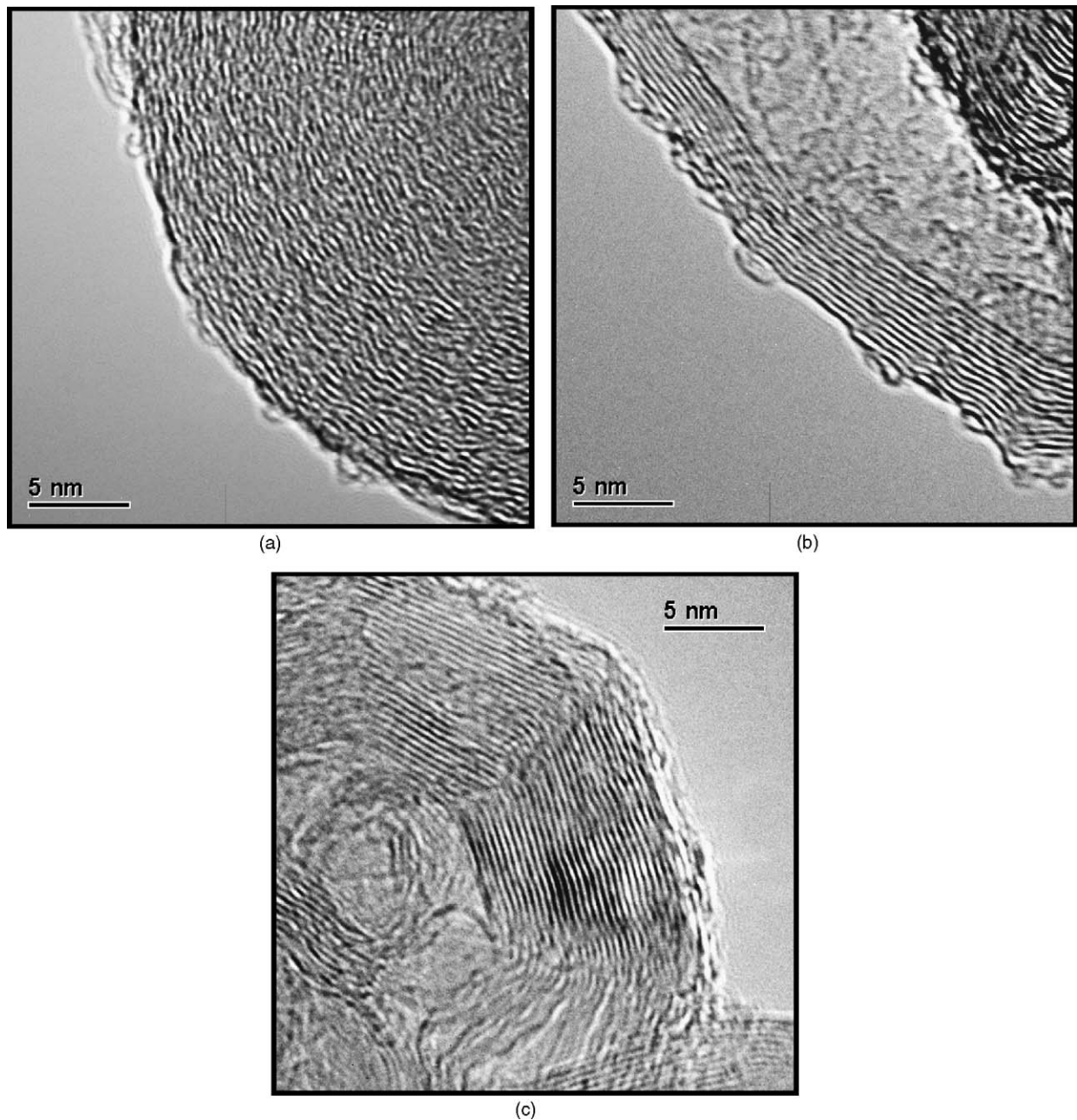


Fig. 1. Transmission electron microscope images: (a) carbon black; (b) acetylene black; (c) graphitized carbon black, PUREBLACK[®] Carbon (manufactured from precursor (a) through graphitization heat treatment).

In accordance with definitions offered by IUPAC, acetylene black is a special type of carbon black formed by an exothermic decomposition of acetylene. It is characterized by the highest degree of aggregation and crystalline orientation when compared with all types of carbon black [16]. In fact, a simple comparison of the TEM images shown in Fig. 1(a and b) allows to draw a conclusion that a typical acetylene black particle (Fig. 1(b)) has much more graphitic structure in its outer crust than that present in a typical particle of carbon black (Fig. 1(a)). The latter particle is composed of randomly oriented graphene planes, which are not aligned parallel to each other, thus manifesting crystalline structure typical of a non-graphitic carbon.

A remarkable observation became the fact that these non-graphitic structures proved to be graphitizable, i.e. they were partially converting into graphite-like structures upon heat treatment at temperatures in the range of 1500–3000 °C.

A TEM image of the heat-treated carbon black from Fig. 1(a) is represented by Fig. 1(c). It is obvious that particles shown in Fig. 1(c), which have been derived from those shown in Fig. 1(a), are more graphitic structures than particles of acetylene black, represented by Fig. 1(b). Though not completely graphitized, the thickness of graphitic shell of new material shown in Fig. 1(c) is at least a factor of 2 higher than that typical of acetylene black.

An unusual parallel stacking of graphene sheets seen in particle shown in Fig. 1(c), along with increased crystallographic order in the third direction (*c*-direction), allowed us to conclude that newly synthesized material is rather unique. We gave a name of PUREBLACK® Carbon to this novel material.

Its existence makes outdated the IUPAC definition for acetylene black (i.e. that portion of it, which states that acetylene black is characterized by the highest degree of aggregation and crystalline orientation when compared with all types of carbon black) [16].

Noteworthy is mentioning that certain partially graphitized forms of carbon and acetylene black have been known in the past. Thus, for instance, references [17,18] describe partially graphitized acetylene black, whose structure has been made more graphitic when a laser beam was directed at the tip of the acetylene torch producing acetylene black-reach smoke. Less exotic methods include batch graphitization of carbon black, which is believed to be very costly and low volume. In contrast, the method of production of PUREBLACK® Carbon, which Superior Graphite is using, is continuous; it was found to be highly efficient, industrial scale, with capabilities of manufacturing in excess of 50,000 tonnes per year, which makes it the first commercial level partially graphitized nano-sized carbon available to the end-users in the industry of power sources.

4.2. Comparison of physicochemical properties of PUREBLACK® Carbon and its ungraphitized carbon black precursor

Fig. 2 offers, for comparison, a set of physicochemical characteristics of PUREBLACK® 315 Carbon versus its non-graphitized carbon black precursor. Noteworthy is mentioning that properties of another grade described in this article, PUREBLACK® 205 Carbon, follow similar trend, and are not therefore shown in Fig. 2.

One can see that properties of carbon black drastically change towards higher purity levels upon graphitization heat treatment. Noteworthy, per definitions of the IUPAC, graphitization heat treatment is defined as a process of heat treatment of a non-graphitic carbon, industrially performed at temperatures in the range between 2500 and 3300 K, to achieve transformation into graphitic carbon [16], though authors have seen conversions of carbon black to graphitic structures begin at much lower temperatures.

As follows from Fig. 2, upon graphitization heat treatment, the value of equilibrium moisture pickup of a carbon material drops by 1250 times. For the final product (in the particular case, this is a grade PUREBLACK® 315 Carbon), it constitutes only 20 ppm, which makes this material very attractive for application in the battery systems with non-aqueous electrolytes, such as, lithium-ion batteries.

On the same chart, one can see that volatile fraction in the structure of carbon black gets reduced from near 10,000 ppm for the precursor to below the detection limit, which our “free volatiles technique” is capable of determining. Though it requires a detailed basic investigation in the future, this phenomenon could probably be explained by low stability of volatile compounds at elevated temperatures, which carbon black is seeing upon graphitization.

Volatile content is usually associated with presence of oxygen-reach surface groups in the carbon macromolecule. Typical oxygen-reach functional groups on carbon edges are: carboxyl, ether, quinone, phenol, carboxylate, aldehyde, lactone, etc. [20].

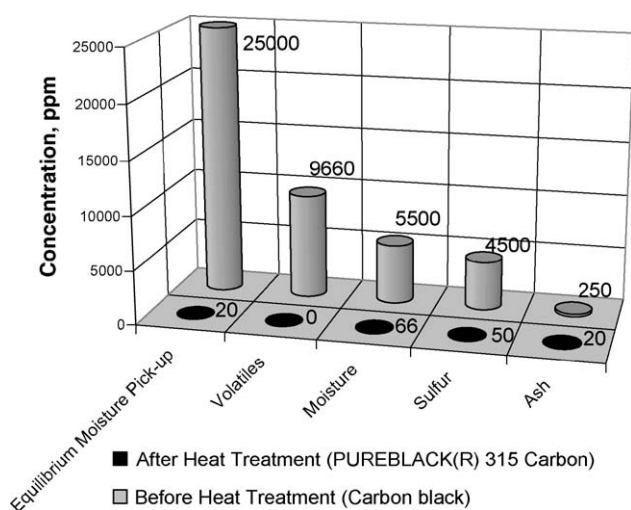


Fig. 2. Comparison of PUREBLACK® 315 Carbon properties and those of its ungraphitized precursor, carbon black.

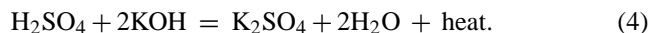
Though generally regarded as impurities, volatiles in carbon structure can do good and bad in batteries. An example of volatile being good is inherent ability of acetylene black to absorb electrolyte (a property of carbon material heavily used in zinc chloride primary cells). At the same time, this same volatile fraction is believed to serve as a site of initiation of a key self-discharge reaction in zinc chloride cells (a phenomenon of thermodynamic decomposition of MnO_2 by the acetylene black, which takes place upon battery storage). This results in a major drawback in performance of commercial zinc chloride primary cells, e.g. short shelf life of this battery system. In Section 4.3, we have provided electrochemical performance data of PUREBLACK[®] 205 Carbon in zinc chloride battery system, where good electrolyte management has been engineered into the cell despite reduced volatility in the carbon material used in the cathode.

Fig. 2 also offers data regarding the reduction of moisture in carbon black before and after its graphitization heat treatment. We would like to note the reduction of moisture in the heat-treated product versus its precursor by more than a factor of 80. The bound moisture level of the heat-treated product, PUREBLACK[®] 315 Carbon, is 66 ppm, as determined by Karl Fischer coulometric titration. This is a lower concentration of bound moisture than that typical of graphite used in lithium-ion battery applications, where excess moisture in cell ingredients may result in reduced abuse tolerance, increased irreversible capacity loss [19], etc., undesirable phenomena.

The next set of bars on a chart shown in Fig. 2 represents results of reduction of sulfur impurities in the carbon black upon its graphitization heat treatment. Since the precursor carbon black is a product of controlled combustion of petroleum oil, it does have sulfur impurities in its composition (4500 ppm in the case of a particular precursor). Upon heat treatment, this number drops down below 50 ppm (a minimal level of detection of the Leco sulfur analyzer used in our investigation).

Residues of sulfur may be irrelevant for certain battery systems, such as, lead acid batteries. However, they were seen to be detrimental in other electrochemical systems. For instance, sulfur in carbon black is viewed as one of the mechanisms of reduction of calendar life of lithium-ion batteries [21]. High sulfur materials with reduced pH are also undesirable in many aqueous electrochemical systems, most of which are based on application of alkaline electrolyte. Thus, it is easy to predict that sulfur in the structure of carbon material, when placed inside electrochemical devices, for instance, in an alkaline battery or into a polymer electrolyte mem-

brane (PEM) fuel cell, may vigorously react with potassium hydroxide electrolyte via reaction of neutralization with the yielding of water:



This reaction will thus dilute electrolyte and possibly catalyze other reactions of self-discharge inside the cell. We are avoiding occurrence of reaction (4) by driving all reasonably measurable sulfur out of carbon material's structure.

One last set of bars represented by Fig. 2 refers to ash. Ash is a summary of mineral impurities in a carbon material. In the corrosive environments inside electrochemical devices (batteries and cells), these impurities may get leached out, and migrate through separator to the opposite electrode, thus catalyzing a number of self-discharge reactions including gassing, which needs to be avoided at any cost due to potential safety hazards and other liability concerns.

Generally, carbon blacks are quite pure. For reference, 250 ppm of ash for precursor carbon black is actually lower than the total amount of mineral impurities in some of the world's most pure graphite sold for energy applications [6,9]. However, the purer they can be, the better.

Even the purest forms of acetylene black [22] and acetylene type carbon black [23] reportedly have too high levels of certain mineral impurities, such as Fe, Mo, Pb, Zn, Ca, etc., which up until now were unavoidable, yet known to be critical impurities responsible for shortening of the battery calendar life.

For instance, it is believed that service life of the lithium/thionyl chloride (Li/SOCl_2) primary batteries [2] can be extended if concentration of Fe gets reduced from currently available 7 ppm (Shawinnigan acetylene black) to lower values. We were able to achieve Fe concentration of 3 ppm with PUREBLACK[®] Carbon (please see a summary in Table 1 with emission spectroscopy data, which lists concentrations of individual impurities in the ash of one of the products of this nature). As one can see from the data presented by Fig. 2, a reduction of total ash by a factor of 10 could be achieved with graphitization heat treatment of a precursor carbon black.

Authors would like to make a comment on the BET surface area changes of carbons before and after they undergo graphitizing heat treatment. Thus, in the case of PUREBLACK[®] 315 Carbon, its surface area changes from approximately $208 \text{ m}^2 \text{ g}^{-1}$ (before heat treatment) to approximately $64 \text{ m}^2 \text{ g}^{-1}$ (in the end-product); in the case of PUREBLACK[®] 205 Carbon, the BET of precursor is in the range of $100 \text{ m}^2 \text{ g}^{-1}$ and it gets reduced to approximate level

Table 1
Emission spectroscopy results of elemental impurities in the ash of PUREBLACK[®] 205 Carbon and PUREBLACK[®] 315 Carbon

	Elemental impurities (ppm)													
	Al	As	Ca	Co	Cr	Cu	Fe	Mo	Ni	Pb	Sb	Si	Sn	V
PUREBLACK [®] 205 Carbon	<5	<1	<10	<1	<1	<1	<3	<1	<1	<1	<1	<5	<1	<1
PUREBLACK [®] 315 Carbon	<3	<1	<12	<1	<1	<1	<3	<1	<1	<1	<1	<5	<1	<1

of $45 \text{ m}^2 \text{ g}^{-1}$. Reduction of surface area upon graphitization is a typical phenomena, which also manifests itself in other forms of synthetic carbons that are subjected to graphitization.

4.3. Comparison of electrochemical properties of PUREBLACK® Carbon and high structure acetylene type carbon black

Carbon black has a fundamental characteristic of its property, known as “structure”. This term is used to describe chain or clustered aggregate formation, and it is measured by standard tests EM (ASTM D3849) and OAN (ASTM D2414) [24]. Structure can be high or low depending on the intended application of carbon black. Conductive applications in the industry of power sources require so-called “high structure” materials, whose macromolecules have multiple “branches” consisting of individual carbon nano-particles. These highly developed nano-sized branches are believed to create additional contact points with active material in electrode matrixes, thus resulting in efficient conductivity enhancement at low concentrations of carbon additives.

For all electrochemical test results described in this section, we used one of the two “high structured” grades of graphitized carbon materials. These are: PUREBLACK® 315 Carbon and PUREBLACK® 205 Carbon. For reference, a TEM of a typical “high structure” macromolecule of one of these grades at different magnifications is represented by Fig. 3. Similar to a particle shown in Fig. 1(c), we would like to note very unusual appearance of the graphitic structures shown in Fig. 3. Noting their graphite-like composition (at a given particle size of below 100 nm), one should expect to see them as being more conductive than traditional forms of acetylene type conductive carbon black.

4.3.1. Illustrative example of application of a PUREBLACK® Carbon in the alkaline-manganese dioxide primary cells

Fig. 4 offers galvanostatic discharge curves of LR2016 coin cells of electrochemical system $\text{Zn}|\text{KOH}, \text{H}_2\text{O}(\text{ZnO})|\text{MnO}_2(\text{C})$. Variable in experiments was the type of carbon used in the EMD cathode. Specific concentrations of carbon with EMD shown in the captions represent the lowest practically advisable ratios after which, for one reason or another, it is no longer efficient to use a particular form of carbon material. Obviously, the overall goal is to use as little amount of carbon material as possible without sacrifice of electrochemical performance of the full cell. This is due to the fact that carbon material performs a function of conductive additive, and any extra amount will result in unnecessary uptake of the valuable space inside the cell.

Modern high quality alkaline primary batteries traditionally employ graphite for conductivity enhancement purposes in the cathodes. Decades ago, this electrochemical system

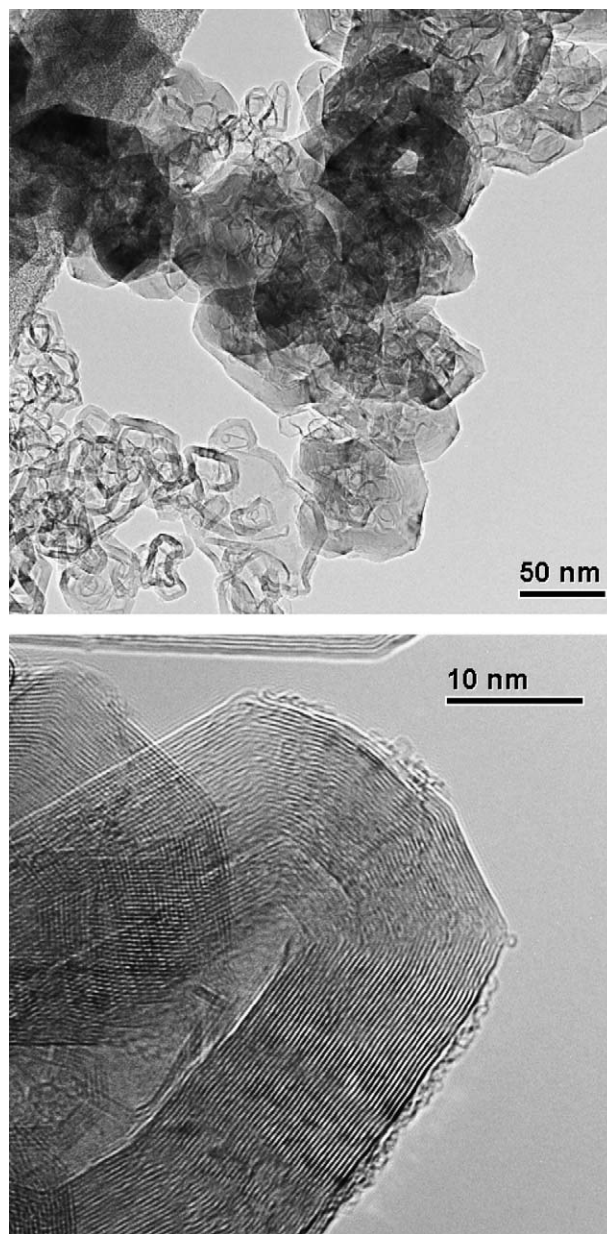


Fig. 3. Transmission electron microscope images of PUREBLACK® 315 Carbon's microstructure at different magnifications.

used acetylene black but then it was determined that due to high volatiles in this type of carbon material, the couple MnO_2 –acetylene black was thermodynamically unstable. As a result, acetylene black has been phased out and replaced with high purity graphite, a solution, which allowed keeping cathodes stable for at least five years. Nowadays, only minute amounts of acetylene black may be added to the cathodes in very special cases, when giving an immediate boost to performance of alkaline batteries is needed. However, this is more an exception than common practice.

In Fig. 4, cells “D” and “B” represent two well-known graphite baselines. The “D” curve corresponds to a battery, which used the alkaline battery grade of synthetic graphite

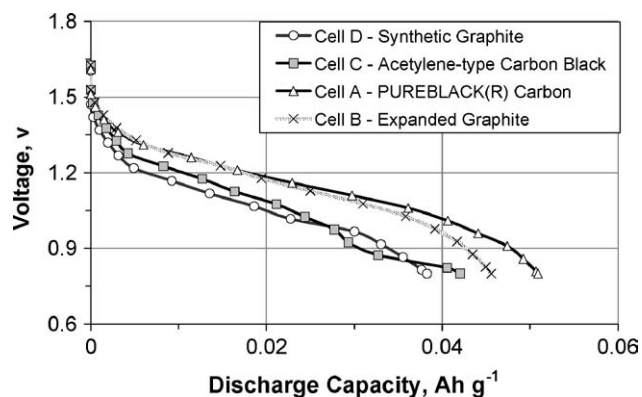


Fig. 4. Galvanostatic discharge curves of LR2016 coin cells (alkaline-manganese dioxide primary system) at the current density of 100 mA per 1 g of EMD: cell A—cell containing 5 wt% of PUREBLACK[®] 315 Carbon with EMD; cell B—cell containing 5.5 wt% of expanded graphite FormulaBT ABG1025 with EMD; cell C—cell containing 5 wt% of Super S (acetylene type conductive carbon black) with EMD; cell D—cell containing 7 wt% of synthetic graphite KS-15 with EMD.

KS-15, available from Timcal, a Swiss company. It is established by the industry that the loading of this graphite should not be less than 7 wt% with EMD, otherwise rapid reduction in cell performance should be expected. Cell “D”, when discharged at high drain continuous discharge of 100 mA per 1 g of EMD from o.c.v. to 0.8 V, gave capacity of 38.3 mAh g⁻¹. Cell “B” used a so-called “expanded” graphite [8], grade FormulaBT ABG1025, available from Superior Graphite. Expanded graphite is a new generation of premium performance graphitic carbon, which may be effectively used at much lower concentrations with EMD than the earlier considered synthetic baseline “D”. In cell “B”, we had to use only 5.5 wt% of FormulaBT ABG1025 with EMD and this cell gave a capacity of 45.6 mAh g⁻¹ at the above high drain (for reference, this is 16% more than capacity of cell “D”).

Discharge curve marked as cell “A” corresponds to a battery that had PUREBLACK[®] 315 Carbon (Superior Graphite) in the cathode. Its concentration was as low as 5 wt% with EMD. At high drain, the cell demonstrated a specific capacity of 50.0 mAh g⁻¹, which even outperformed cell based on expanded graphite—a state-of-the-art conductive additive.

We speculate that it is due to a synergistic effect of graphitic structure (which make it more conductive in matrixes) and finer particle size (which adds contact points with active material) that PUREBLACK[®] 315 Carbon outperforms expanded graphite. A classical line of thought, however, would be to suggest that matrixes having PUREBLACK[®] Carbon are more conductive because of this material’s higher surface area and finer particle size. We dispute this approach to explaining high conductivity, and as evidence, would like to refer to discharge curve “C” in Fig. 4. This curve stands for a battery, which used acetylene type conductive carbon black (Grade Super S), Timcal, Belgium. This material is sold for conductivity enhancement purposes in batteries with aqueous electrolytes. In the particular test,

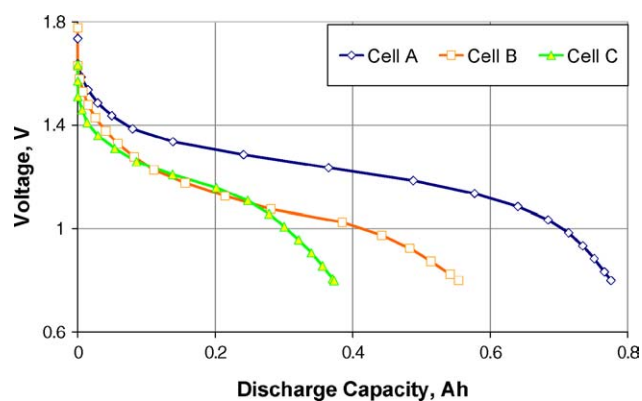


Fig. 5. Galvanostatic discharge curves of zinc chloride AA (R6) batteries at the current density of 100 mA per cell: cell A—cell based on 8 wt% of PUREBLACK[®] 205 Carbon in the cathode; cell B—cell having 8 wt% of AB55, a “dry cell” grade of Shawinningan acetylene black; cell C—commercial baseline “Q-FORCE Super Extra Heavy Duty”, a product of People’s Republic of China.

we used 5 wt% of Super S with EMD. Noteworthy, particle sizes of PUREBLACK[®] 315 Carbon and Super S are similar (30–100 nm range); at the same time, the surface area of Super S is higher than that of expanded graphite by a factor of 2. Despite, upon discharge, the “C” cell gave only 42 mAh g⁻¹, which is 8.8% better than performance of a cell based on synthetic graphite KS-15, but 7.9% worse than performance of a cell based on expanded graphite FormulaBT ABG1025, and 16% worse than what a cell based on PUREBLACK[®] 315 Carbon has demonstrated.

From all materials studied in this set of experiments, PUREBLACK[®] 315 Carbon proved to be most efficient conductive additive.

4.3.2. Illustrative example of application of a PUREBLACK[®] Carbon in the zinc chloride batteries

Fig. 5 offers for comparison three discharge curves of AA size zinc chloride batteries. These cells were discharged from their o.c.v. to a cut-off voltage of 0.8 V at a high drain current density of 100 mA per cell. Two longer lasting batteries correspond to cells made at Superior Graphite’s Peter R. Carney Technology Center. The discharge curve with worst performance (cell C) corresponds to a commercial AA cell, purchased in a retail store in greater Chicago, IL, at the same time the internally produced cells were being made. The commercial cell has a name of “Q-FORCE Super Extra Heavy Duty”, a product of People’s Republic of China.

First of all, the authors were pleased to conclude that we can build much better zinc chloride batteries than those being sold in the stores in Chicago. The AA size Q-Force battery gave 372.7 mAh at 100 mA continuous discharge per cell. The second best electrochemical device (cell B) turned out to be an internally built AA cell, which had 8 wt% of AB55, a “dry cell” grade of Shawinningan acetylene black available from CP Chem, Houston, TX [22].

This cell gave 554.3 mAh, which is as much as 32.8% better than performance extracted from the Q-FORCE battery. Though one needs to note that difference in performance is significant only below 1 V, when the battery is about to die. Also, the AB55-based cell had a characteristic drop in discharge voltage, which may indicate limited ability of acetylene black to support discharge with high current densities.

The best result (cell A) has been obtained for an AA cell, which incorporated 8 wt% of PUREBLACK® 205 Carbon in the cathode. We were able to extract 775.6 mAh from this cell at 100 mA continuous discharge. The only difference between this and the previous cell was the type of carbon used in the cathode, and the fact this led to 28.5% improvement in the performance of full cell at high drain.

As a processing comment, we need to note that amount of electrolyte absorbed by PUREBLACK® Carbon will differ from the amount of electrolyte absorbed by acetylene black. Thus, in electrolyte, which we used in this study (40 wt% ZnCl₂, 0.5 wt% NH₄Cl and 0.25 wt% ZnO), the cathode based on acetylene black AB55 absorbed 25% of moisture, while the cathode based on PUREBLACK® 205 Carbon absorbed only 18%. On the other hand, we have also noticed that with PUREBLACK® 205 Carbon, due to its higher packing density, one can put in 15.7% more of active material into the same volume of a cell than what could be achieved with acetylene black AB55.

The above results create prerequisites for application of PUREBLACK® Carbons in the zinc chloride primary batteries, which is absolutely the largest segment of the worldwide battery market in terms of number of cells being made. Specifically, this market is estimated to be at 20 billion cells per year and it is predicted to grow by 3–4% annually [1]. Analysis of results shown in Fig. 5 further suggests that PUREBLACK® Carbons may allow significant upgrading of quality of zinc chloride cells in the foreseeable future. Making “dry cells” last as long as alkaline primary batteries (shelf life improvement), and even making them compete with some of alkaline cells performance wise (in medium and low drain applications), is not out of reach for a skilled battery engineer.

4.3.3. Illustrative example of application of a PUREBLACK® Carbon in the lithium/manganese dioxide battery system

In order to be able to assess performance of the PUREBLACK® Carbons in non-aqueous battery systems, we have assembled an “upgraded” version of Li/MnO₂ primary cells with chief experimental variable being the type of carbon used in the cathode.

By “upgrading”, we mean application of a non-traditional electrolyte (taken from lithium-ion technology), i.e. the system we have built was as follows: Li|LiPF₆ (EC:DMC)|MnO₂ (C) versus the classic set up of Li|LiClO₄ (PC: DME)|MnO₂ (C). In our opinion, presence of a different electrolyte does not diminish significance of the results,

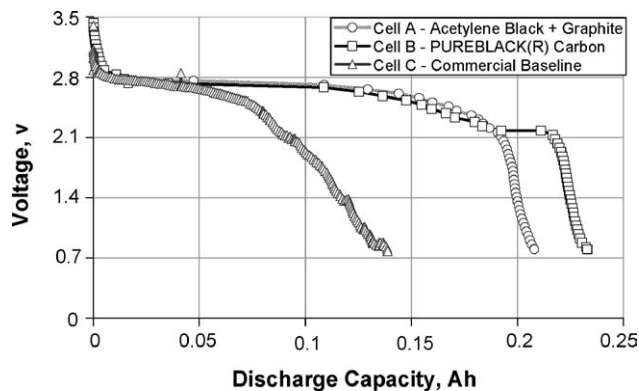


Fig. 6. Galvanostatic discharge curves of lithium/manganese dioxide CR2325 cells at the current density of 1 mA per cell (11.2 k Ω): cell A—cell with 8 wt% carbon materials in the cathode, 4 wt% AB55 (CP Chem’s Shawinigan acetylene black) and 4 wt% of graphite FormulaBT EBG2620 (Superior Graphite); cell B—cell with cathode incorporating 5 wt% of graphitized carbon black, PUREBLACK® 315 Carbon; cell C—commercial CR2325 baseline (low rate Li/MnO₂ primary cell manufactured by the Generator Battery Plant in Kiev, Ukraine).

which have been presented by Fig. 6, and summarized in the sections below.

Fig. 6 shows three discharge curves, one of which (“C”) belongs to discharge of commercial CR2325 low rate Li/MnO₂ primary cells (manufactured by the Generator Battery Plant in Kiev, Ukraine). Two remaining curves (“A” and “B”) correspond to the CR2325 Li/MnO₂ primary cells assembled at Superior Graphite’s Peter R. Carney Technology Center).

Typically, the cathodes of Li/MnO₂ cells contain 8–12 wt% of conductive carbon additives [25]. Often, such additives are 1:1 blend of graphite and acetylene black. We have constructed cell “A” with 8 wt% carbon materials in the cathode. The composition was: 4 wt% AB55 (CP Chem’s Shawinigan acetylene black) and 4 wt% of graphite FormulaBT EBG2620 (Superior Graphite). Cell “B” used only 5 wt% of graphitized carbon black, PUREBLACK® 315 Carbon.

Cells “A”, “B” and “C” were discharged at “high” rate (1 mA per CR2325 cell, which corresponds to approximately 11.2 k Ω). Commercial cells (similar to “C”) have also been discharged with a low rate of 0.5 mA per cell (not shown in Fig. 6). Upon “low” rate of discharge, commercial cells gave capacity of 176.5–180 mAh at 2 V. In general, the meaningful results of discharge are those, which cover the range from cell’s o.c.v. to a cut-off voltage of 2 V. This chemistry is not being used at voltages below 2 V.

Noteworthy is the fact that typical rated capacity for commercial CR2325 cells is in the range of 0.17–0.19 Ah per this size cell. Such measurements are taken at much lower drain rate ($C/200$), and besides, our test results can also be referenced to [2]. In this regard, rated capacity of Generator’s CR2325 cells is very consistent with capacity ratings described in the literature.

Considering the above “industry standard” capacity values, we have been able to obtain much better performance in our internally made cells. Specifically, cells A based on a blend of graphite and acetylene black gave capacity of 194.4 mAh (note the discharge was done at approximately twice higher current density than the rated capacity at which the industry is producing their capacity values). At this same high drain rate of 1 mA per unit, cell B (based on 5 wt% PUREBLACK[®] 315 Carbon) gave as much as 219.8 mAh. For reference, commercial cell “C” at this current density gave capacity of 98.3 mAh.

The above data allow drawing conclusion that with the new form of graphitized carbon black (particularly with PUREBLACK[®] 315 Carbon), one can achieve very significant improvement in Li primary battery performance at the account of reduction of the amount of carbon material needed in the cathode matrix, and due to higher conductivity of this material.

4.3.4. Outlook for application of PUREBLACK[®] Carbons in other electrochemical systems

Though we limited this paper to only few practical examples of how application of the newly developed form of partially graphitized carbon black, PUREBLACK[®] Carbon, can improve overall battery performance, we are certain that engineers skilled in the art of electrochemical power sources will be able to take the above data and apply it towards improvement of systems they work on. Authors, in the mean time, are continuing their studies of behavior of PUREBLACK[®] Carbon in fuel cells, electrochemical ultracapacitors, zinc air cells, lithium-ion batteries, etc.

Examples of performance observations with PUREBLACK[®] Carbon in the cathodes of the lithium-ion batteries, which we have seen so far, include high conductivity, increased stability at elevated voltages (especially needed in LiMn₂O₄ and other spinel-based chemistries), ease of processing, ability of NMP-based slurries containing cathode active material and PUREBLACK[®] Carbon to stay suspended without a need for additional mixing before coating onto current collectors (apparently due to enhanced abilities of PUREBLACK[®] Carbon to act as good dispersing agent), and other outstanding properties suggesting that this new form of carbon material deserves evaluation by the industry.

5. Conclusions

Graphitization heat treatment of carbon black was seen to effectively produce a wide variety of forms of partially graphitized nano-sized carbonaceous materials with a set of unique properties. The authors call these novel materials PUREBLACK[®] Carbons.

TEM images of particles of PUREBLACK[®] Carbon highlight more graphitic structures than particles of acetylene black. Though not completely graphitized, the thickness of graphite-like outer shell in the new material is at least a factor

of 2 more than that typical of acetylene black. Appearance of newly developed structures reveals an unusually looking parallel stacking of graphene sheets along with increased crystallographic order in the third direction (*c*-direction), which, as authors proposed, results in increased conductivity.

Heat treatment, besides graphitization, was seen to dramatically purify nano-carbon materials under investigation. Thus, a reduction of total ash by a factor of 10 could be achieved with graphitization heat treatment of a precursor carbon black. As a result, concentration of Fe in ash was reduced to below 3 ppm with PUREBLACK[®] Carbon, while best industry baseline, Shawinnigan acetylene black, is available at concentrations of down to 7 ppm. In the considered example, authors have indicated that with PUREBLACK[®] Carbon's low Fe content, it may be possible to extend service life of the lithium/thionyl chloride primary batteries.

The bound moisture level of the heat-treated product was found to be only 66 ppm, as determined by Karl Fischer coulometric titration. This was explained to be a very low value and should offer advantages in lithium-ion battery applications (excessive moisture in non-aqueous electrolyte systems may result in reduced abuse tolerance, increased irreversible capacity loss, etc.).

Galvanostatic discharge curves of LR2016 coin cells of electrochemical system Zn|KOH, H₂O (ZnO)|MnO₂ (C) revealed that at high drain rates of 100 mA g⁻¹ of EMD, the cell demonstrated a specific capacity of 50 mA g⁻¹, which outperforms cell based on expanded graphite—a state-of-the-art conductive additive for alkaline battery technology. We speculate that this is due to a synergistic effect of graphitic structure (which makes it more conductive in matrixes) and finer particle size (which adds contact points with active material) that PUREBLACK[®] Carbon outperforms expanded graphite, synthetic graphite and acetylene black.

Galvanostatic discharge curves of AA size zinc chloride batteries from their o.c.v. to a cut-off voltage of 0.8 V at a high drain current density of 100 mA per cell revealed that the best result has been obtained for an AA cell, which incorporated 8 wt% of PUREBLACK[®] 205 Carbon in the cathode. We were able to extract 775.6 mAh from this cell, while similarly made cells which used acetylene black performed 28.5% worse at this high drain regime of discharge.

Illustrative example of application of a PUREBLACK[®] Carbon in the lithium/manganese dioxide battery system also led to promising results with the newly developed carbon material. Thus, typical rated capacity for commercial CR2325 cells is in the range of 0.17–0.19 Ah per CR2325. These measurements are taken at low drain rate of about 0.5 mA per cell. We found that at twice higher current density (1 mA per CR2325), cell based on 5 wt% PUREBLACK[®] 315 Carbon gave as much as 219.8 mAh, while commercially available cells at this current density gave capacity of only 98.3 mAh.

While authors continue their basic investigation on behavior of various PUREBLACK[®] Carbons in fuel cells, electrochemical ultracapacitors, zinc-air cells, lithium-ion batteries,

etc., emerging systems, the new materials discussed in this work are already available to battery engineers in the approximate amount of 50,000 tonnes per year.

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