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Fluorinated Coal Derived Carbons and Electrodes for Use in Battery Systems and Similar

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(54) **FLUORINATED COAL DERIVED CARBONS AND ELECTRODES FOR USE IN BATTERY SYSTEMS AND SIMILAR**

(58) **Field of Classification Search**
CPC .. H01M 4/1393; H01M 4/382; H01M 4/5835;
H01M 4/625; C01B 2202/20; C01B
31/0253

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See application file for complete search history.

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(21) Appl. No.: **15/592,510**

Li, et al, The tunable electrochemical performances of carbon fluorides/manganese dioxide hybrid cathodes by their arrangements. Journal of Power Sources 274 (2015) 1292-1299.

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(Continued)

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Related U.S. Application Data

Primary Examiner — Brittany L Raymond

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(74) *Attorney, Agent, or Firm* — King & Schickli, PLLC

(51) **Int. Cl.**

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H01M 4/38 (2006.01)
H01M 4/583 (2010.01)
H01M 4/587 (2010.01)
H01M 4/62 (2006.01)
H01M 4/1393 (2010.01)

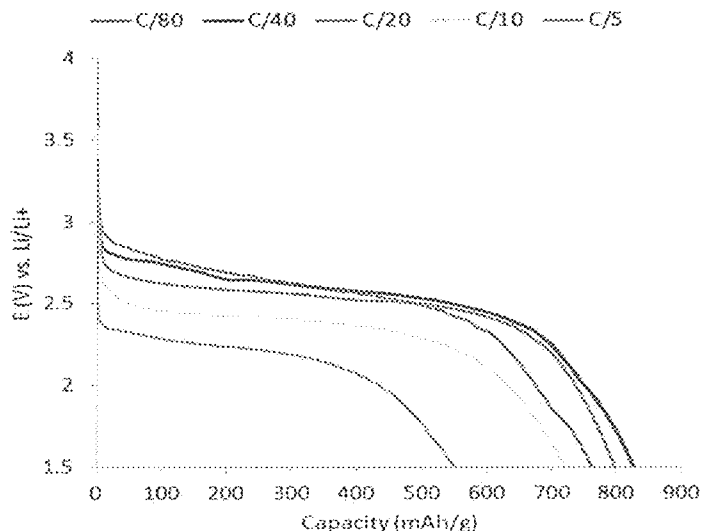
(57) **ABSTRACT**

An electrode including fluorinated and surface defluorinated coal is described, as well as methods of producing such and employing such within an electrical system. The coal in the electrodes is fluorinated at an amount of between 0.3 and 1.4. The resulting coal products can be further surface defluorinated and maintain functionality within an electrical system.

(52) **U.S. Cl.**

CPC **H01M 4/5835** (2013.01); **H01M 4/1393** (2013.01); **H01M 4/382** (2013.01); **H01M 4/625** (2013.01); **C01B 2202/20** (2013.01)

9 Claims, 7 Drawing Sheets



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FIGURE 1

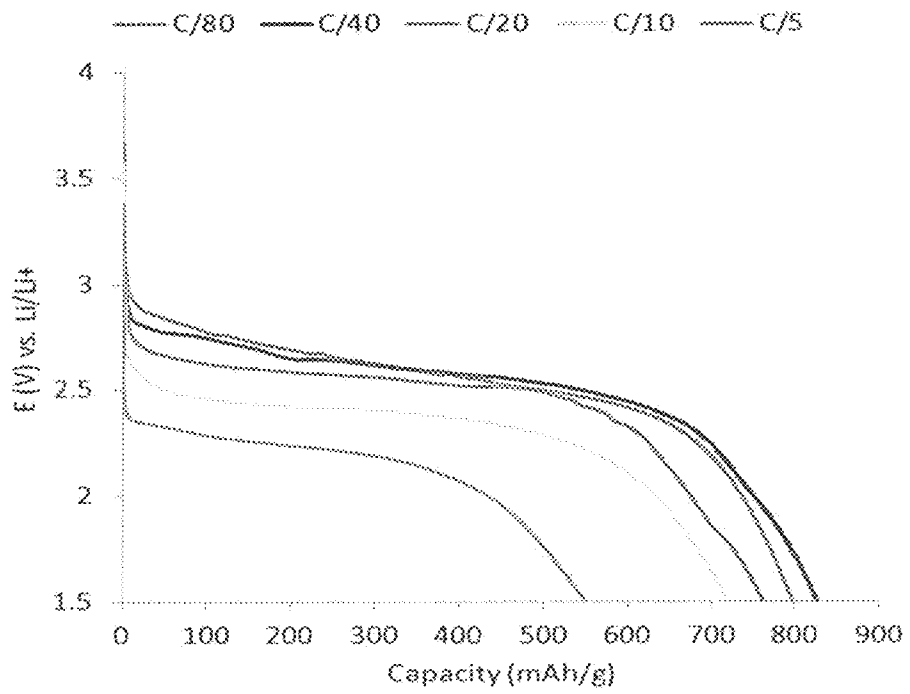


FIGURE 2

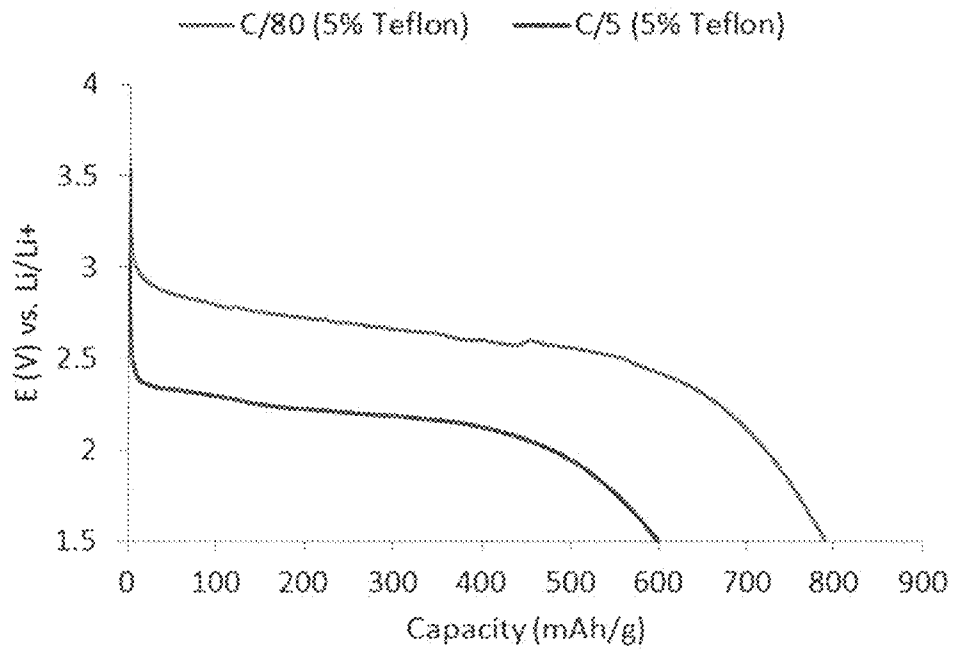


FIGURE 3

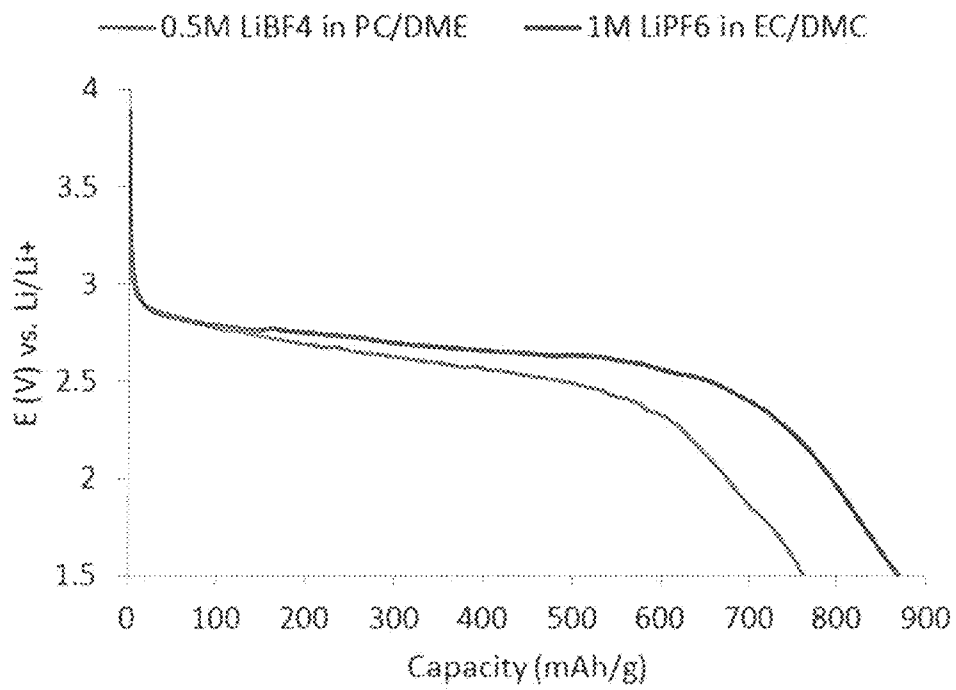
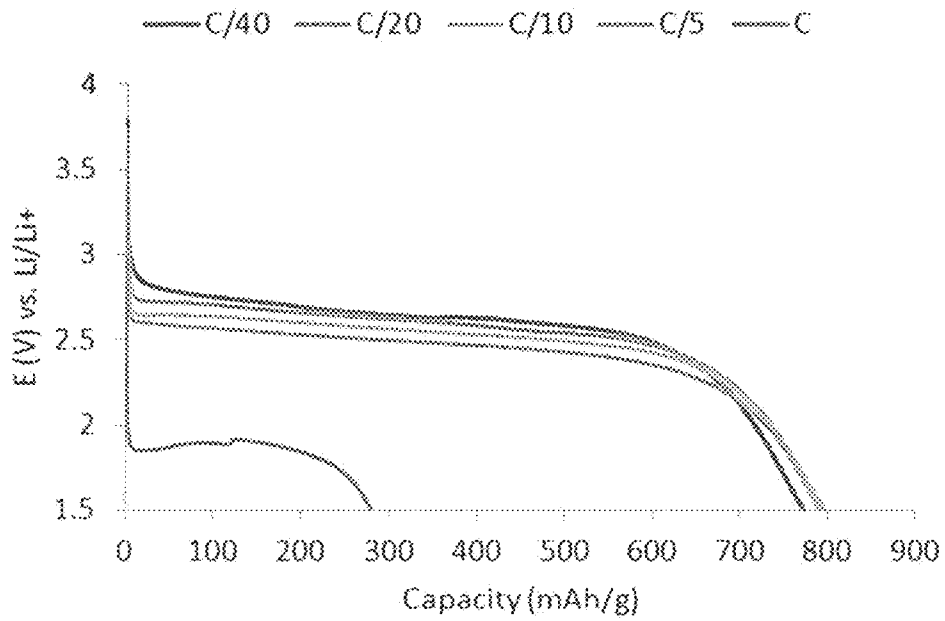


FIGURE 4



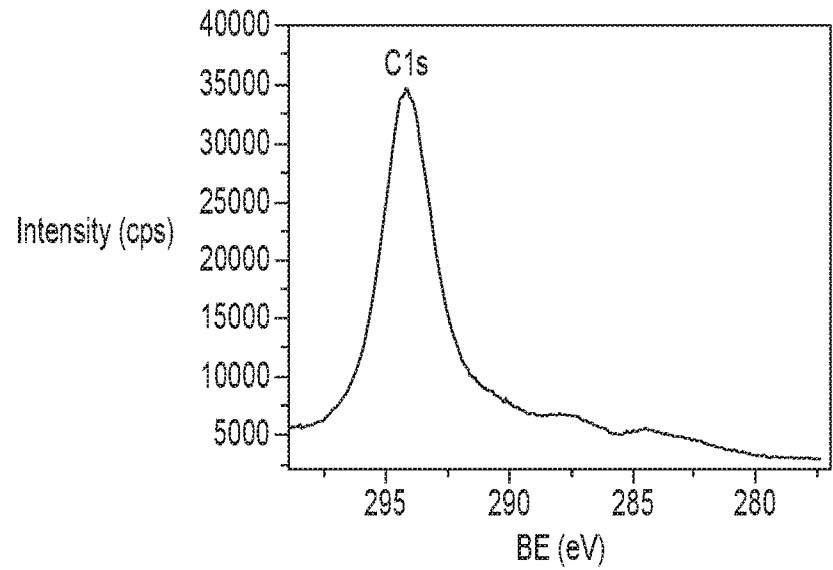
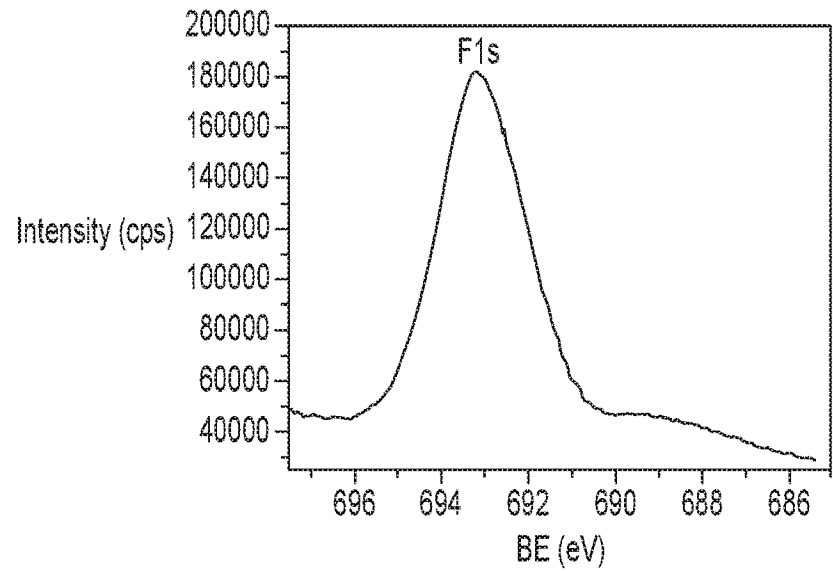
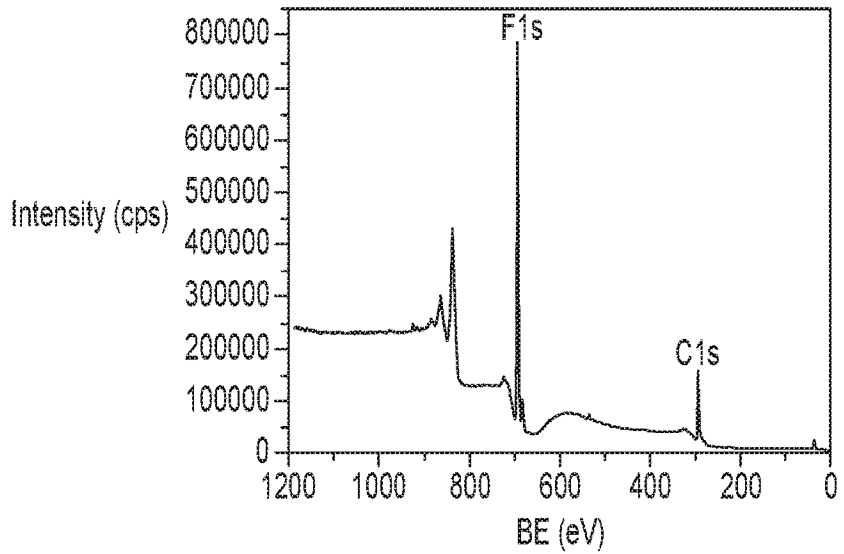


FIG. 5

FIGURE 6

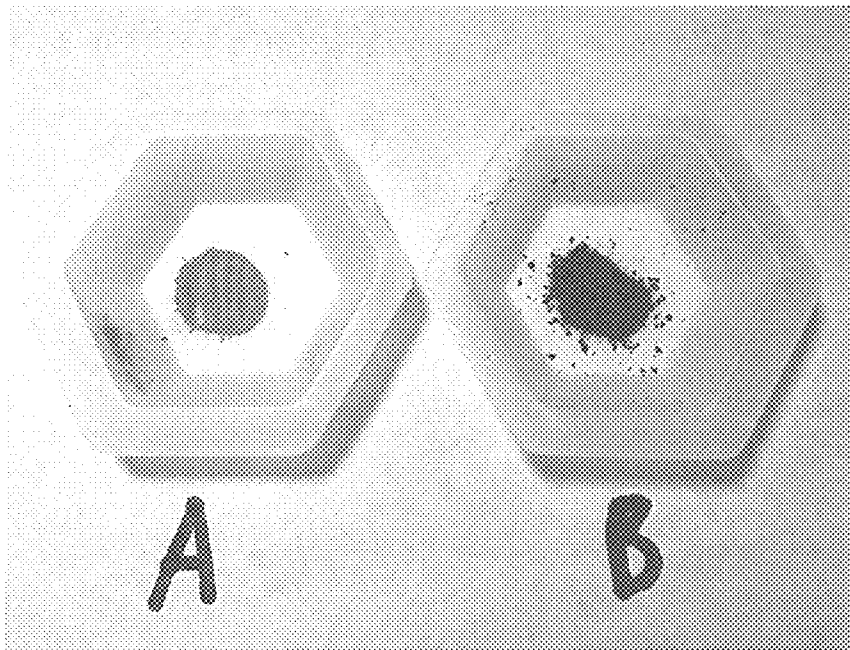
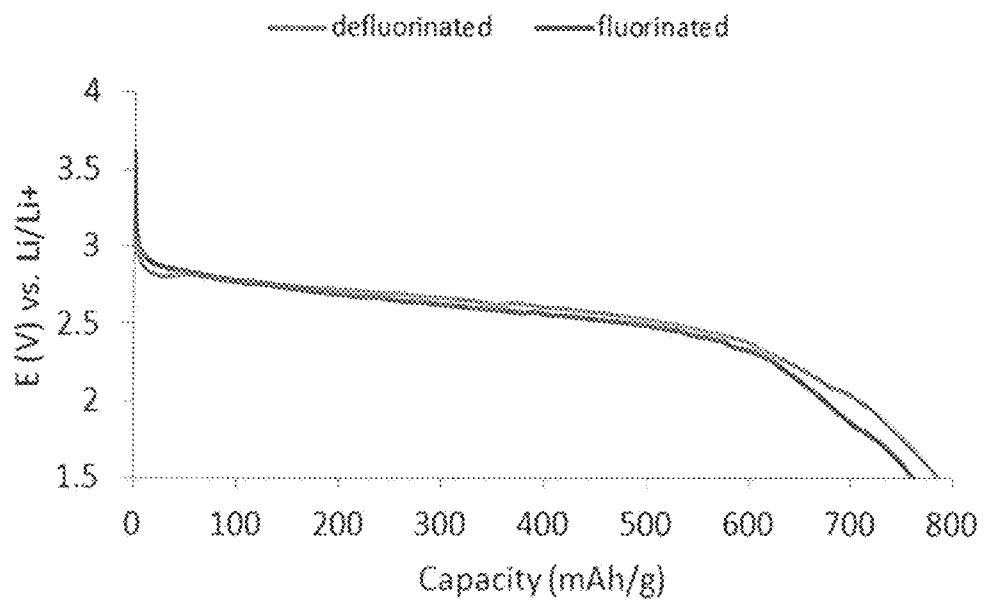


FIGURE 7



FLUORINATED COAL DERIVED CARBONS AND ELECTRODES FOR USE IN BATTERY SYSTEMS AND SIMILAR

RELATED APPLICATION

This application claims priority to U.S. Provisional Application 62/334,770, filed May 11, 2016, which is hereby incorporated by reference in its entirety.

TECHNICAL FIELD

This document relates to electrodes composed of fluorinated and surface defluorinated coal, as well as to electrical systems utilizing said electrodes.

BACKGROUND SECTION

Carbon is an attractive material for use within lithium battery systems to the accepted standard of manganese dioxide due to the potential to improve performance. However, costs associated with developing fluorinated carbon particles have to date hindered any practical development for the consumer market making them cost prohibitive.

Coal is an abundant source and cheap source of carbon, but other elements present within coal render it impractical as a viable carbon source for many commercial applications. The costs associated with purifying carbon from coal similarly hinder the use coal. In electrical systems, carbon is abundantly utilized for its conductive properties. With coal, however, the presence of other elements, such as sulphur, nitrogen, oxygen and hydrogen are too disruptive to allow coal to be utilized. The present invention has identified an approach that nullifies these adverse effects and allows coal to function as a carbon source in electrical applications.

SUMMARY OF THE INVENTION

In accordance with the purposes described herein, the present invention provides in part for a composition of fluorinated coal particles. The coal particles include fluorinated carbon that is fluorinated at a ratio of between about 0.3 and 1.4 to 1 carbon. The coal particles may have a mean width of about 400 nm and 20 μ m.

In some embodiments, the coal particles may further have their exterior surface defluorinated.

The present invention also provides for an electrode formed from the coal particles. The electrode may be formed with a binder. In some embodiments, the coal particles may form a hybrid electrode with MnO_2 (manganese dioxide) and SVO (silver vanadium oxide).

The present invention also provides for a battery system with a cathode comprised of the fluorinated and/or surface defluorinated coal particles described herein. The battery system may use a lithium or sodium based electrolyte, along with a corresponding lithium or sodium based anode.

The present invention also provides in part for methods of formulating the coal particles described herein, comprising grinding coal to a particulate, filtering to select the desired width range of particles, heat treating and fluorinating. The methods may further comprise defluorinating the exterior surface of the coal particles.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawing figures incorporated herein and forming a part of the specification, illustrate several

aspects of the present embodiments and together with the description serve to explain certain principles of those embodiments. In the drawings:

FIG. 1 shows the discharge performance of fluorinated anthracite coal ($CF_{1.09}$) at five different discharge rates, including C/80, C/40, C/20, C/10, and C/5. The electrolyte was 0.5M $LiBF_4$ in 2:8 PC/DME, and the electrode composition was 85% $CF_{1.09}$, 5% carbon black, and 10% Teflon 6C.

FIG. 2 shows two discharge curves of fluorinated anthracite coal ($CF_{1.09}$) at two different discharge rates (C/80, C/5). The electrolyte was 0.5M $LiBF_4$ in 2:8 PC/DME, and the electrode composition was 85% $CF_{1.09}$, 10% carbon black, and 5% Teflon 6C.

FIG. 3 shows a comparison of two discharge curves (discharge rate=C/80) for fluorinated anthracite coal ($CF_{1.09}$) in two different electrolytes; 0.5M $LiBF_4$ in PC/DME, and 1M $LiPF_6$ in EC/DMC. the electrode composition was 85% $CF_{1.09}$, 5% carbon black, and 10% Teflon 6C.

FIG. 4 shows the discharge performance of fluorinated anthracite coal ($CF_{1.09}$) in 1M $LiPF_6$ (EC/DMC) at five different discharge rates: C/40, C/20, C/10, C/5, and C. The electrode composition was 85% $CF_{1.09}$, 5% carbon black, and 10% Teflon 6C.

FIG. 5 shows data obtained by XPS (x-ray photoelectron spectroscopy) that was used to determine the elemental composition of the fluorinated anthracite coal. The elemental composition was determined to be $CF_{1.09}$.

FIG. 6 shows comparative images of fluorinated coal particles (FIG. 6A) and surface defluorinated coal particles (FIG. 6B).

FIG. 7 shows a comparative graph of capacity and voltage discharge between fluorinated and defluorinated coal particles within lithium battery systems.

Reference will now be made in detail to the present preferred embodiments, examples of which are illustrated in the accompanying drawings.

DETAILED DESCRIPTION

The present invention provides for fluorinated and surface defluorinated coal particles. The process of fluorination is established, see, e.g. Ahmad, Y. et al. *Carbon*. 2015, 94, 1061. The particles can have a mean diameter of between about 400 nm and 20 μ m. The particles may be prepared by mining coal or obtaining mined coal, grinding the coal into particulate, heat treating the particulate coal in an inert atmosphere, such as N_2 or Ar, and then fluorination. Following fluorination, the CFx coal particles can optionally undergo solvothermal treatment to remove excess F from the exterior surface of the coal particles to improve performance. The coal particles can be derived from anthracite, bituminous and sub-bituminous coals or combinations thereof. Following grinding, the coal particles may be optionally selected for a desired average width, such as between about 400 nm and 20 μ m.

The present invention provides, in part, for fluorinated coal particles (CFx coal particles), wherein the particles are fluorinated at a ratio to carbon of between about 0.3 and 1.4 to 1. For example, the coal particles may comprise between about $CF_{0.3}$ to $CF_{1.4}$. In some instances, the coal particles may comprise about $CF_{1.09}$. Fluorination of the coal particles can be controlled by the amount of reaction time, as well as other components, such as concentration of reactant fluoride, temperature, pressure and volume of the reaction.

The fluorinated coal particles may be further surface defluorinated. Based on the CF_x coal particles synthesized as described herein, an optional surface de-fluorination process under mild hydrothermal condition may be applied to further modify the surface of CF_x coal particles used to prepare electrodes. (see, e.g., Dai, Y. et al. *Journal of Materials Chemistry A*. 2014, 2 (48), 20896-20901.). The fluorination of coal particles is complete throughout the particle. However, as noted in the demonstrations described herein, surface defluorination of the coal particles can offer further advantages while still providing the advantages observed with the fully fluorinated product. This optional step doesn't significantly affect the overall mass, but may further improve the high rate performance of the electrode by removing excess, low conductivity F from the surface of the coal particles, thereby rendering them more conductive and dramatically improving the discharge rate. Thus, surface defluorination of coal particles can improve performance when used as a cathode in a battery system, such as in a Li-CF_x or Na-CF_x battery described herein.

The present invention also provides for electrodes comprising the fluorinated and/or surface defluorinated coal particles described herein. The particles can be formed into an electrode of a desired shape and utilized in a battery system. The electrodes may further comprise a binder such as Teflon to hold the particles together. The binder may be present at between 3 and 15 weight percent of the electrode. Other binder materials such as PVdF (polyvinylidene fluoride) and CMC (carboxymethyl cellulose) can be used.

The coal particles described herein can also be formed in a hybrid cathode formulation (or mixture) containing CF_x-MnO₂ and/or CF_x-SVO (silver vanadium oxide) and operated as a primary battery containing a lithium (Li) or sodium (Na) based battery anode. The ratio or mixture of materials in the cathode would depend for the most part on the desired application. Mixtures of MnO₂ and CF_x are becoming commonplace and are also driven by cost (CF_x is expensive compared to MnO₂ but has higher capacity). MnO₂, present in a battery system in the form of nanowires, provides a higher discharge rate performance than CF_x, for example. CF_x and mixtures with MnO₂ and SVO provide an option to get the best of all materials, namely achieving both high energy and high power. In the case of a hybrid cathode, the maximum capacity of the electrode is the sum of the individual capacities and the mix ratio is the mix ratio is the ratio of the individual capacities, such that the cathode capacity is equal to $C_{total} = (C_{MnO_2} \times W_{MnO_2} + C_{CF_x} \times W_{CF_x}) / (W_{MnO_2} + W_{CF_x})$; where, W_{MnO_2} and W_{CF_x} are the mass of the MnO₂ and CF_x cathode materials, respectively.

The hybrid cathode may further comprise additional features such as a binder and/or other carbonaceous material, e.g. CNTs, graphene, hydrothermally dehydrated carbon particles. Collectively, the CF_x and MnO₂ and/or SVO may comprise between 80 and 90% by weight of the cathode. The CF_x may comprise between about 20 to 95% by weight of the cathode. MnO₂ and/or SVO may comprise between about 20 to 80% by weight of the cathode (see, e.g., US Pub. App. 20150311532, incorporated by reference herein in its entirety).

The Li-CF_x and Na-CF_x batteries are exemplary types of battery system that offers very high-energy density, long-storage life, very good safety record, a wide temperature operating range, and very low self-discharge. For example, Li-CF_x batteries possess the highest theoretical energy density among commercially available primary lithium batteries at 2180 Wh/kg, with a long storage life of >20 years, low

self-discharge rate of <0.5% per year, and wide temperature operating range between -40° C. and 170° C.

The CF_x coal particles may further be combined with other carbonaceous material in forming an electrode, such as activated carbon, carbon nanotubes, graphite, graphene, hydrothermally dehydrated carbon and fullerenes. The CF_x coal particles may be utilized in one or both electrodes within a battery system. The battery system may utilize a lithium or sodium based electrolyte. The battery system may use either lithium-based electrolytes for Li-CF_x, and sodium-based electrolytes for Na-CF_x primary batteries. Typical salts that can be utilized in these systems include LiBF₄, LiPF₆, and NaPF₆. Typical organic solvents that are employed in these systems include carbonates (ethylene carbonate, dimethyl carbonate), esters (methyl propionate, γ-butyrolactone), ethers (1,2-dimethoxyethane, 1,3-dioxolane), and other polar solvents (dimethylsulfoxide, acetonitrile). In addition, ionic liquids can also be utilized as electrolytes for primary Li-CF_x or Na-CF_x battery systems under higher temperature conditions (see Madria, N. et al. *Journal of Power Sources*. 2013, 234, 277-284.)

Utilization of the CF_x coal particles as an electrode or part thereof within a battery system provide capacities much higher than the sum value of each component measured at the same rate. For example, a hybrid CF_x coal particle/other carbonaceous (e.g. carbon nanotubes (CNTs)) material cathode within a Li-MnO₂ nanowire battery system integrates both the superior rate performance of MnO₂ nanowires and the higher specific capacity of CF_x active materials, and avoids shortcomings, such as low discharge rate capability and voltage delay (see, e.g., Kijima et al., *J. Solid State Chem.*, 178: 2741, 2005; and Cheng et al., *Inorganic Chemistry*, 45(5): 2038, 2006). Most importantly, such a hybrid configuration of the cathode greatly improves the high rate discharge performance.

EXAMPLES

Fluorinated coal particles (particle size: 1-10 microns) were prepared by obtaining ground, milled, and previously mined anthracite coal, graphitized (note: the anthracite particles had already been ground and milled to a particle size range of ~1-10 microns, (submicron particles also can be used) and the particles were graphitized in the temperature range of 2000-2700° C. prior to fluorination). at 2000° C. to 2700° C. under argon, and then fluorinated to a C/F ratio of 1/1.244. FIG. 6(a) shows images of fluorinated CF_{1.09} coal particles. The particles can further be defluorinated. according to the methodology of Dai et al., by heating fluorinated anthracite coal in alkaline ethanol/water mixtures at 180° C. for 1-2 hours. FIG. 6(b) is an image of defluorinated CF_{1.09} particles. The defluorination as per Dai, et. Al., was used but we believe that there are hydrothermal conditions (T, chemistry, etc.) that would work as well but have not explored these. The CF_x particles were determined to be fluorinated at a ratio to carbon of 1.09:1. [The degree of fluorination is a function of the reaction conditions utilized during the fluorination process, including fluorination temperature, time, and ratio of fluorine gas to carbonaceous material]. The CF_x coal particles were formed into electrodes with 10% Teflon as a mechanical binder, and 5% carbon black to serve as a conductive additive and added in the percentages presented in table 1 and assessed in a lithium battery system for capacity and discharge voltage. Table 1, along with FIG. 1, shows that increased CF_{1.09} (fluorinated anthracite coal; 10% Teflon) offers useful discharge capacity and discharge voltage.

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TABLE 1

C rate	Capacity (@ 1.5 V vs. Li/Li+); mAh/g	Avg. discharge voltage (V; vs. Li/Li+)
C/80	762	2.49
C/40	828	2.50
C/20	798	2.50
C/10	719	2.40
C/5	549	2.28

Next, CF_x coal particles were utilized in electrodes with 5% teflon at the percent amount listed in Table 2 and assessed in a lithium battery system. Table 2, along with FIG. 2, shows that the CF_{1.09} (fluorinated anthracite coal; 5% Teflon) offer comparable capacity and voltage discharge despite the halving of Teflon present.

TABLE 2

C rate	Capacity (@ 1.5 V vs. Li/Li+); mAh/g	Avg. discharge voltage (V; vs. Li/Li+)
C/80	791	2.54
C/5	599	2.35

It was next examined how the CF_{1.09} coal particles would perform in the presence of different electrolytes. Table 3, along with FIG. 3, shows that the CF_{1.09} coal particles can achieve higher discharge capacities and higher average discharge voltages in the 1M LiPF₆ electrolyte.

TABLE 3

electrolyte	Capacity (@ 1.5 V vs. Li/Li+); mAh/g	Avg. discharge voltage (V; vs. Li/Li+)
0.5M LiBF ₄	762	2.49
1M LiPF ₆	870	2.56

Table 4, along with FIG. 4, shows CF_{1.09} (fluorinated anthracite coal; 10% Teflon 6C, 5% carbon black) can achieve excellent discharge capacities and average discharge voltages to a discharge rate of C/5, with a noticeable decrease in cell performance metrics at higher discharge rates (C), leading to reduced discharge capacities and average discharge voltage.

TABLE 4

C rate	Capacity (@ 1.5 V vs. Li/Li+); mAh/g	Avg. discharge voltage (V; vs. Li/Li+)
C/40	774	2.57
C/20	799	2.55
C/10	791	2.52
C/5	795	2.48
C	280	2.01

It was next assessed how surface defluorination of the particles would affect capacity and voltage discharge. Table 5, along with FIG. 7, shows a comparison of fluorinated vs. defluorinated coal, demonstrating the surface defluorination can further increase overall performance.

TABLE 5

sample	Capacity (@ 1.5 V vs. Li/Li+); mAh/g	Avg. discharge voltage (V; vs. Li/Li+)
defluorinated	786	2.51
fluorinated	762	2.49

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Table 6 shows the discharge performance characteristics of primary Li cells prepared with a hybrid CF_x/MnO₂ cathode at different compositions. Carbon nanotubes (CNT) are used in the cathode compositions as an additional conductive additive. The cathode compositions are given in terms of weight % of each component and the CNTs are held constant at 10% for each cathode formulation. The discharge rates range from C/5 to 5C. These data illustrate what effect the various ratios of MnO₂ and CF_x have on capacity, energy density and power density. Coal fluorinated and surface defluorinated particles, given their comparable performance would be expected to provide similar results.

TABLE 6

Discharge Characteristics						
Cathode Composition	C Rate	Current (mA)	Mean Point Voltage (V)	Capacity (mAh/g)	Energy Density (Wh/kg)	Power Density (W/kg)
MnO ₂ : 63%	C/5	99.3	2.34	424	992	232
CF _x : 27%	1C	496	2.11	344	726	1047
CNT: 10%	2C	993	2.04	330	673	2026
<i>C_{Theory}</i> :	3C	1489	1.94	288	559	2889
496.4	4C	1986	1.87	269	503	3714
mAh/g	5C	2482	1.74	259	451	4319
MnO ₂ : 45%	C/5	124	2.31	460	1063	286
CF _x : 45%	1C	622	2.10	421	884	1306
CNT: 10%	2C	1244	2.03	390	792	2525
<i>C_{Theory}</i> :	3C	1866	1.94	386	749	3620
622 mAh/g	4C	2488	1.74	335	583	4329
	5C	3110	1.63	280	456	5069
MnO ₂ : 27%	C/5	150	2.40	593	1423	360
CF _x : 63%	1C	748	2.11	548	1156	1578
CNT: 10%	2C	1495	2.02	503	1016	3020
<i>C_{Theory}</i> :	3C	2243	1.99	475	945	4464
747.6	4C	2990	1.86	442	822	5561
mAh/g	5C	3738	1.67	270	451	6242

The foregoing has been presented for purposes of illustration and description. It is not intended to be exhaustive or to limit the embodiments to the precise form disclosed. Obvious modifications and variations are possible considering the above teachings. All such modifications and variations are within the scope of the appended claims when interpreted in accordance with the breadth to which they are fairly, legally and equitably entitled. All literature cited herein, including patent and non-patent literature is hereby incorporated by reference in its entirety.

What is claimed:

1. An electrode comprising fluorinated coal particles, wherein said particles comprise fluorinated carbon at a ratio of between about CF_{0.3} and CF_{1.4}.
2. The electrode of claim 1, wherein the mean width of said particles is between about 400 nm and 20 μm.
3. The electrode of claim 1, wherein the exterior surface of said particles is defluorinated.
4. The electrode of claim 1, further comprising a binder.
5. The electrode of claim 1, further comprising MnO₂ (manganese dioxide) and SVO (silver vanadium oxide).
6. A battery system comprising the electrode of claim 1.
7. The battery system of claim 6, further comprising a lithium or sodium based electrolyte.
8. The battery system of claim 6, wherein the electrode is a cathode.
9. The battery system of claim 6, further comprising an anode comprised of lithium or sodium.