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LDRD PROJECT NUMBER: 184519

LDRD PROJECT TITLE: Tunable Graphitic Carbon Nano-Onions Development in Carbon Nanofibers for Multivalent Energy Storage

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ABSTRACT:

We developed a novel porous graphitic carbon nanofiber material using a synthesis strategy combining electrospinning and catalytic graphitization. RF hydrogel was used as carbon precursors, transition metal ions were successfully introduced into the carbon matrix by binding to the carboxylate groups of a resorcinol derivative. Transition metal particles were homogeneously distributed throughout the carbon matrix, which are used as *in-situ* catalysts to produce graphitic fullerene-like nanostructures surrounding the metals. The success design of graphitic carbons with enlarged interlayer spacing will enable the multivalent ion intercalation for the development of multivalent rechargeable batteries.

INTRODUCTION:

High performance rechargeable batteries are the key enablers for electric vehicles and smart grids in the 21st century, driven by the rapidly expanding energy demands. The initiative to develop multivalent-ion (MV-I) batteries (Mg, Ca, Al) is to elaborate a competitive battery technology for higher volumetric energy density, owing to the greater number of electrons transferred per metal-cation. Alkaline metals are naturally abundant and inherently safer than Li. Using the alkaline metals or alloys as anodes via deposition-dissolution theoretically yields higher energy density, however such anodes suffer inhibited cation transmission due to surface passivation, or poor lifetime due to volume expansion. For example, fully-reversible Mg anodes and Chevrel phase-based high-rate Mg cathodes[1] have been successfully proved, however after more than a decade, no Mg rechargeable battery based on a Mg metal anode is ready for commercialization. The performance limits are the unacceptable energy density suffering from low working voltage and limited capacity of the cathode, which are imposed by the incompatibility between conventional electrolytes and metal anodes.[2, 3] Conventional electrolytes cannot be used in Mg rechargeable batteries, because a thermodynamically stable Mg^{2+} blocking layer is formed on Mg metal surface making the anode function irreversibly. The current state-of-the-art organohaloaluminate electrolyte allows reversible electrodes, however its extremely narrow electrochemical window (~ 2 V vs. Mg/Mg^{2+}) limits the operation voltage and the choice of cathode materials. To date, no reversible, efficient, extended life-cycle MV-I battery has been achieved despite significant efforts placed on metal anode surface control through electrolyte development.

Intercalation anodes involving host materials would have to bear some loss in energy density due to the host penalty; however they will negate the surface passivation challenges since no formal electron transfer is required. Instead, they would enjoy precision, reliability, and enhanced safety, as demonstrated in the highly successful Lithium Ion Batteries (LIB). This would simplify the electrolyte design such that conventional electrolytes may be used instead. The resulting carbon host would be less active electrochemically than when charged with Li, with great promise to partner with the emergent high voltage cathode (3~5 V). Furthermore, intercalation anode cell designs can benefit from lessons learned from LIB refined in the past 20 years, therefore the translation error can be minimized at system level[4]. Graphite is the host materials in LIB, however it is unsuitable for MV-I intercalation because the limited interlayer-spacing poses hurdles for intercalation due to the multivalent nature of the cations (high charge/radius ratio). Our overarching research goal is to develop internally-nanostructured carbon materials with an expanded interlayer-spacing, to determine the structure-intercalation activity relationships, and to create the fundamental understanding necessary to establish the limits of MV-I intercalation.

In order to validate MV-I intercalation anode chemistry and create fundamental understanding necessary to establish the limits of MV-I intercalation, we propose to develop novel classes of internally nanostructured carbon materials with tailored (expanded) interlayer-spacing as anode material. MV-I graphite intercalation compounds can be formed by vapor phase treatment, suggesting that MV-I intercalation is not limited by thermodynamics but rather by the energetics and kinetics of MV-I delivery to and into the host. Expanded graphitic interlayer-spacing is expected to positively impact the intercalation energy barrier and solid-state diffusion of MV-I within the carbon. The rationale is that the host materials should matter for intercalation: a) Tuning of the solid electrolyte interphase (SEI) could increase the interfacial mobility, as electrolyte decomposition electrochemistry is substrate (electrode) material-dependent; b) Wider channels should improve the solid-state diffusion kinetics. c) Built-in wider spacing decreases the van der Waals attraction between graphene sheets that must be partially negated to enable MV insertion.

Specifically in this Exploratory LDRD, We propose to focus on developing novelty carbon nanofibers with graphitic carbon nano-onions structures via a scalable electrospinning approach, together with a catalytic graphitization strategy. These graphitic carbon nanofibers will contain fullerenic nanostructures with expandable and tunable graphitic interlayer spacing that allows reversible MV-I intercalation. Such electrically-conductive novel carbons will be used as intercalation anode materials, with high surface areas and open accessible porosities that can minimize the diffusional resistance.

DETAILED DESCRIPTION OF EXPERIMENT/METHOD:

We used a strategy involving both electrospinning and catalyst-assisted graphitization. We propose to introduce nanometer sized transition metal particles (e.g. Ni, Fe, Co...) into the carbon precursors and have them distributed throughout the carbon matrix, then form nanofibers via electrospinning, followed by *in-situ* catalytic graphitization at temperatures around 1000 °C. Electrospinning readily produces amorphous carbon nanofibers, which are normally fully graphitized at temperatures > 2000 °C to form densified carbon fibers. In the transition metal doped carbon matrix, these metallic particles induce a solid state restructuring of the surrounding carbon into graphitic layers. Therefore within the framework of carbon nanofibers are nanometer-sized graphitic nano-onions consisting of concentrically layered graphene shells resembling fullerene structure. The proposed strategy is illustrated in **Figure 1**.

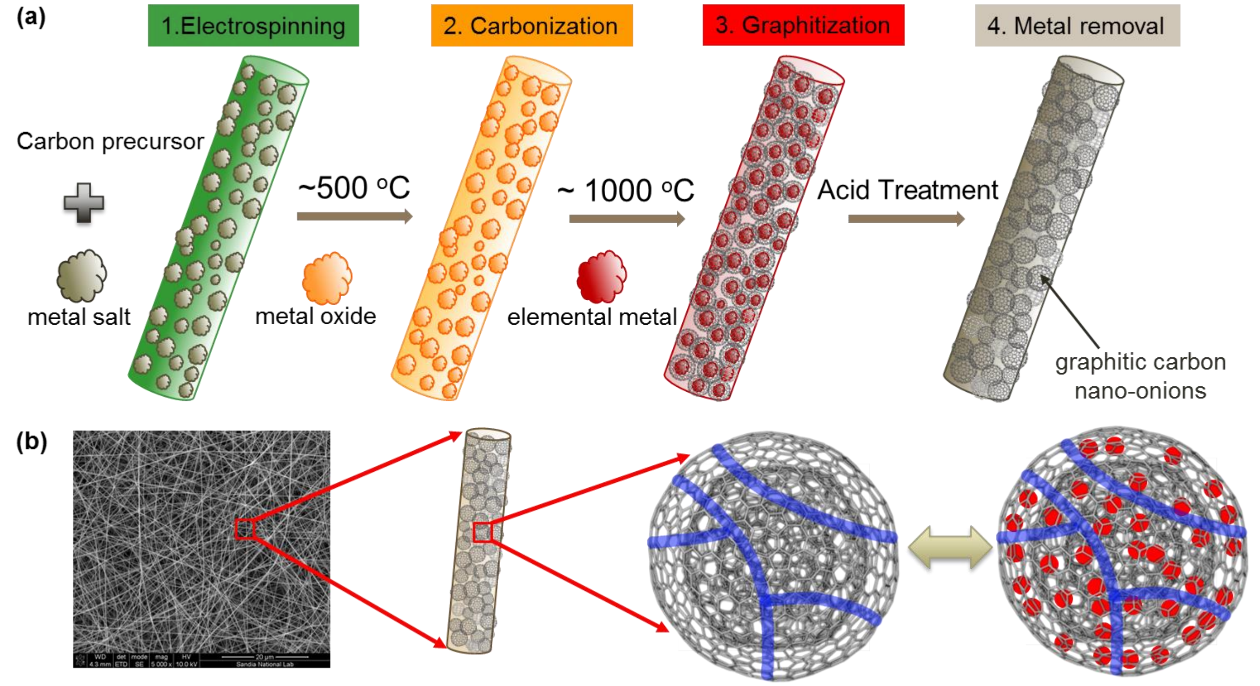

Figure 1 Schematics of ultraporous graphitic carbon naonfibers synthesis strategy.

(a) Use a combined electrospinning (for fiber morphology) and *in-situ* catalytic graphitization (for internal graphitic nano-onion structures) strategy;

(b) Exploded views of the graphitic nano-onion structured that are embedded within the fibers. Defects (blue cracks) inherently exist due to low temperature graphitization process. In the onion-like fullerenic nanostructures, the metal ions proposed in multivalent batteries, such as Mg (red dots), get to be reversely intercalated into the graphitic interlayer spacing.

In order to synthesize carbon nanofibers doped with transition metal as graphitization catalysts, our strategy includes the following steps:

1. Sol-gel polymerize formaldehyde (F) and resorcinol (R) derivatives, the potassium salt of 2, 4-dihydroxybenzoic acid (DHBA);

2. Electrospin this K^+-doped RF gel into nanofibers, then cure the nanofibers;
3. Emerge the K^+-doped RF nanofibers in transition metal salt solutions for ion-exchange. Since the K^+-doped RF gel contains metal-binding moieties, the K^+ will be replaced by transition metal ions;
4. Reduce the transition metal ions to transition metal oxide at carbonization temperature of 500^oC;
5. The carbons will be graphitically catalyzed by the *in-situ* transition metals to produce onion-ring fullerenic nanostructures at 1050 ^oC;
6. The graphitic interlayer spacing can be further tuned by oxidation and reduction.

Sol-gel materials Preparation

We used sol-gel precursors of resorcinol derivative DHBA (R) and formaldehyde (F) to produce K^+-doped RF gel materials. In a typical experiment, 5.8 g (37.6 mmol) of DHBA was added in 200 ml of distilled water, immediately treated with 2.6 g (18.8 mmol) of potassium carbonate (K_2CO_3) under vigorous stirring (600 rpm). The solution became clear in 0.5 hour, after the acid was completely being neutralized by the base. A 25 ml out of the 200 ml of the DHBA- K_2CO_3 solution was mixed with 0.76 g (9.4 mmol) of formaldehyde in a sealed bottle to cure at the room temperature for 24 hours. The molar ratio used to make this derivative RF gel is DHBA: K_2CO_3: Formaldehyde = 1: 0.5: 2.

Electrospun precursor carbon nanofibers

In order to assure a stable electrospinning to happen, we added 4% Polyvinylpyrrolidone (PVP, Mw=1,300,000) into the RF gel precursor. The PVP was well mixed into RF gel precursors at an elevated temperature of 50^oC for 1 hr under 600 rpm stirring. Surfactant Triton X-100 was also used to improve the electruspun nanofiber quality. We electrospun the RF gel-PVP mixture using a 25 Gauge metallic needle connected to a 5 ml syringe at a high voltage of 14.6 KV DC. The feedthrough pumping rate was 0.5 ml/hr. The cathode and anode distance in the electrospinning setup was 15 cm. The electrospun K^+-doped RF hydrogel nanofibers were collected and attached tight to the aluminum foil, and they were cured at room temperature for 24 hr, followed by at 80^oC (Yamato DKN-402C convection oven) for 48 hr.

Ion-Exchange for transition metal ions

K^+-doped RF hydrogel nanofibers were emerged in 0.1 M aqueous solution of $M(NO_3)_2$ (where M is Ni, Co, or Cu) for ion-exchange. During 24 hr period of time, fresh transition metal salt solution was provided for 3 times. The resultant samples were soaked and washed in distilled water for 5 times in 24-hr duration, and finally was washed in acetone to remove all the water.

Carbonization and graphitization

Transition metal doped hydrogel fibers were carbonized at 500^{o}C for 3 hrs in a high temperature vacuum furnace (Lindburg BlueM 1700C tube furnace). Further graphitization at 1050^{o}C under inert condition will be performed in the future due to the furnace broke-down.

Materials characterization

Scanning electron microscopy (SEM) was performed on a FEI Nova NanoSEM operated at 15 kV, with a Backscatter Detector (vCD). Elemental analysis was performed on TEAM Pegasus Integrated EDS (Energy dispersive spectroscopy) Octane Plus detector by EDAX. High resolution transmission electron microscopy (HR-TEM) was performed on FEI Tecnai F30 TEM operated at 300 kV for bright field imaging, and under Scanning transmission electron microscopy (STEM) mode for dark-field imaging.

RESULTS:

RF hydrogel nanofiber synthesis

K^+-doped RF gel was prepared by polymerizing a resorcinol derivative, DHBA together with K_2CO_3, with formaldehyde, using potassium carbonate as a basic catalyst. Under the alkaline conditions, the R and F components reacted and formed the cross-linked gel network. The resultant RF hydrogels in conjunction with Polyvinylpyrrolidinone (PVP) were electrospun into precursor carbon nanofibers that were collected on Aluminum foil. It was challenging to obtain a stable electrospinning condition with the RF gel, even with the presence of PVP. Many beads formed and spread across the nanofibers as beads-on-a-string structures. After 1% Triton X-100 was added to the spinning solution, the fiber quality was dramatically improved. The carbon precursor fibers were continuous with diameters ranging between 100~200 nm. We used SEM to examine the morphology of the carbon precursor fibers. The SEM micrographs in **Figure 2** show nanofiber mats could be produced by electrospinning, and the significant improvements on fiber morphology after using surfactant.

After ion exchange and wash, the carbon fiber morphology was maintained, confirmed by SEM. EDS mapping data suggested that the transition metal ions successfully replaced the K^+ after ion exchange. An example of elemental mapping after exchanging Ni^{2+} for K^+ is shown in **Figure 3**Figure 3. Carbon was eliminated from the mapping for clarity. The Aluminum signal came from the foil. The Platinum signal came from the thin film coating that was sputtered on for imaging purpose. K element existed as a minor background instead attaching to any particular regions, but Ni element strongly appeared in fibers regions.

The EDS elemental analysis was used to evaluate transition metal doping efficiency via ion exchange. The results confirmed that Co^{2+} and Ni^{2+} successfully replaced almost all K^+

respectively within the carbon precursor nanofibers, as shown in **Figure 4**. The carboxylate moiety in the DHBA serves as the metal binding sites responsible for incorporating metal species into the carbon gel framework, therefore K^+ could be replaced by other transition metal ions through the diffusion-limited ion-exchange process. In the pristine K^+-doped RF nanofibers (Figure 4-a), only K appeared in the energy spectrum. After ion-exchange with the transition metal salt solution of Co and Ni, K^+ was successfully replaced by Co^{2+} and Ni^{2+} respectively. Co (Figure 4-b) and Ni (Figure 4-c) signature peaks appeared in the corresponding energy spectrum, but with almost undetectable K.

Graphitic carbon fiber formation

PVP is not a carbon precursor under N_2 atmosphere, instead it decomposes and disappears at a lower temperature of 400 ^oC, which made the RF hydrogel the only carbon precursor. Under thermal treatment at 500 ^oC in an inert atmosphere, transition metal Ni species were uniformly distributed throughout the carbon fiber matrix, with particle size in the tens of nanometer range, see **Figure 5**. Due to the large differences in atomic numbers (Z) between Ni and C, the Ni species stood out in the carbon fibers, as shown in both the bright field and dark field TEM micrographs. There was unfortunately no time to conduct X-ray diffraction yet to confirm the exact crystalline structure of the Ni particles. They are expected to restructure the surrounding carbon into graphitic nano-onions at the next step of higher temperature treatment (~1150^{o}C) in an inert atmosphere.

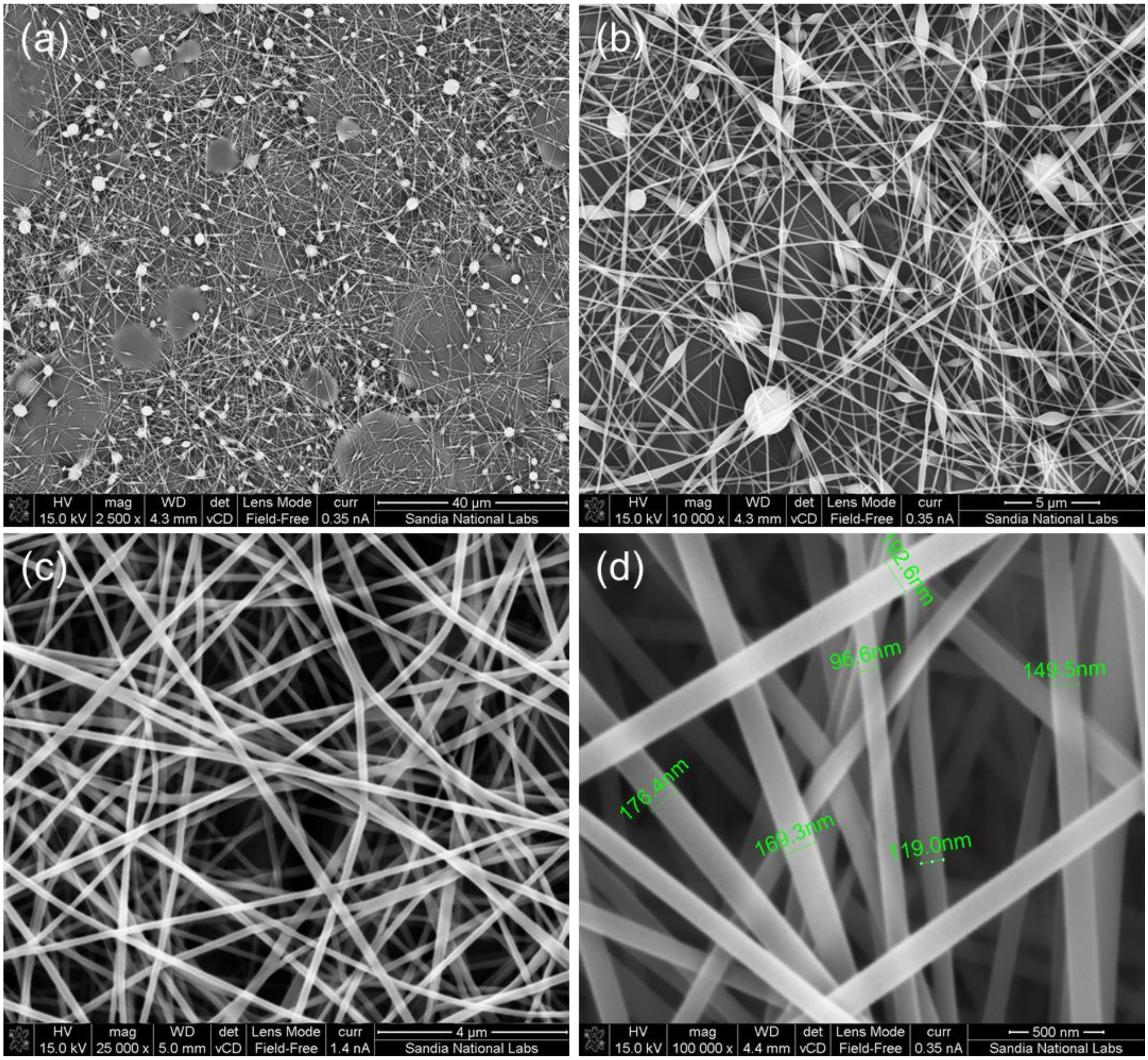

Figure 2 SEM characterization of the K-doped RF hydrogel nanofibers. (a) and (b) RF gel with 4% PVP was used as the electrospinning source materials, with beads-on-a-string morphology due to the unstable electrospinning condition; (c) and (d) After 1% Triton X-100 was added to the source solution, the fiber quality was dramatically improved.

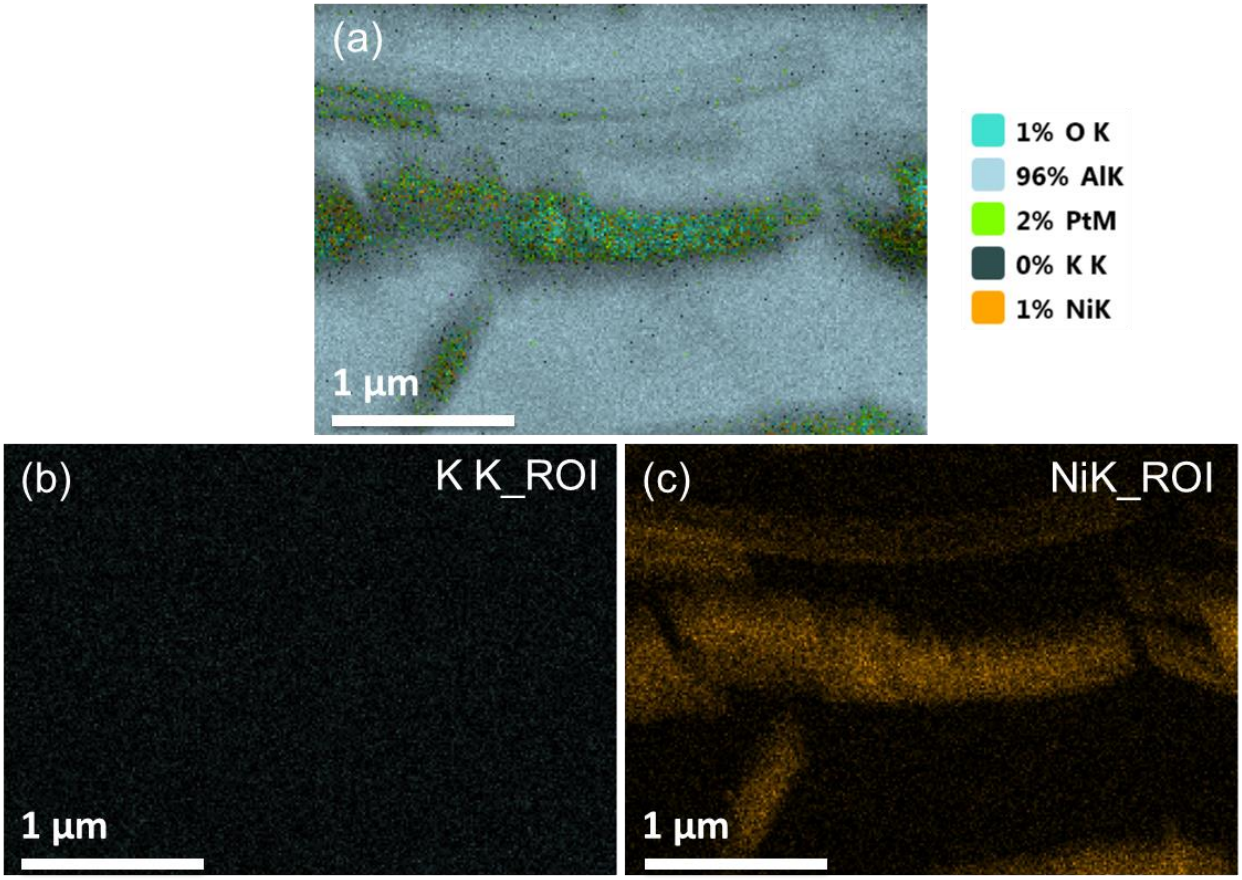

Figure 3 EDS elemental mapping suggested that Ni successfully replaced K via ion-exchange. (a) Major elements overlay on top of each other; (b) K element existed as a minor background instead attaching to any particular regions; (c) Ni element strongly appeared in fibers regions.

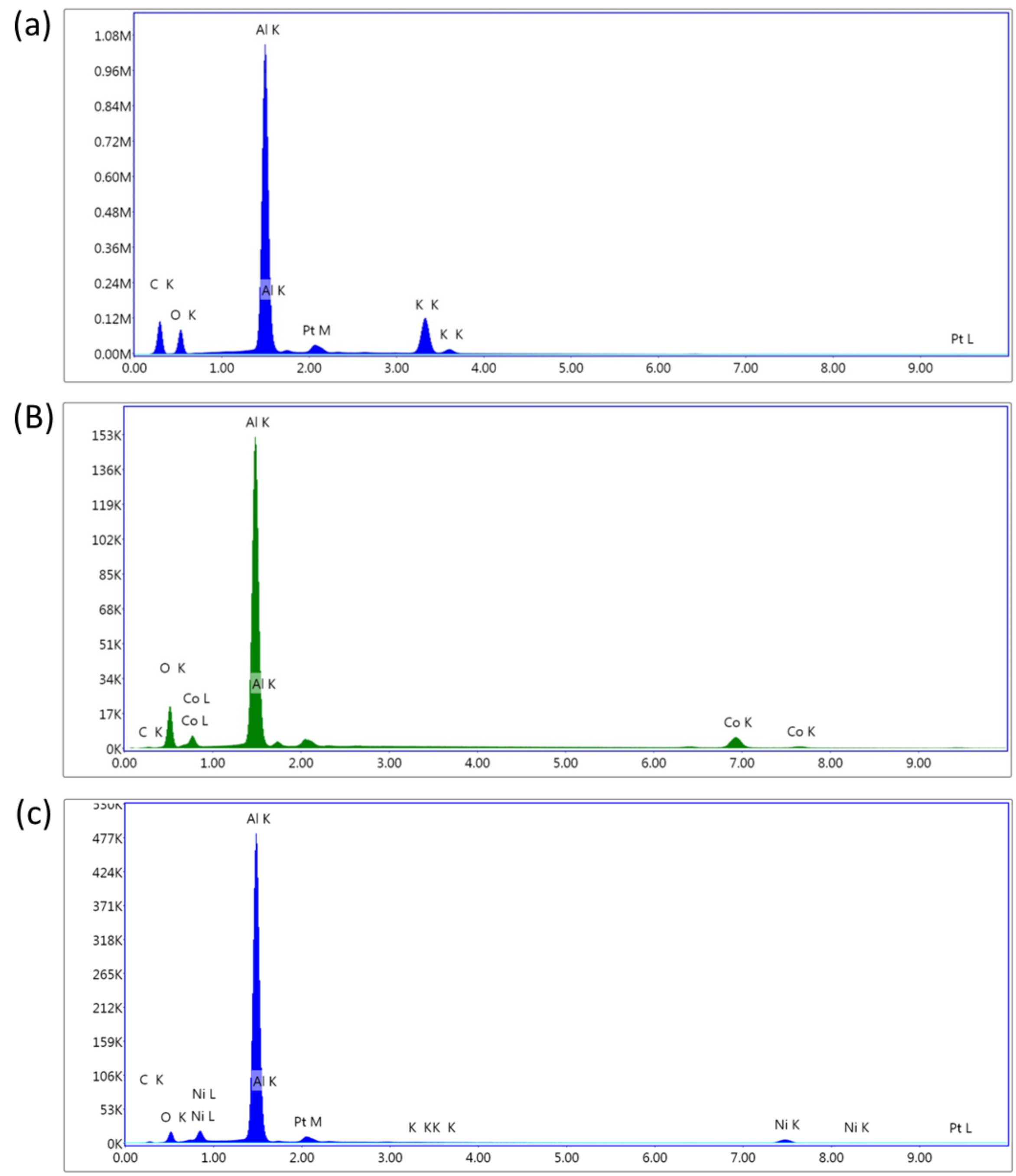

Figure 4 Elemental analysis evaluation confirmed that Co^{2+} and Ni^{2+} successfully replaced almost all K^{+} respectively within the carbon precursor nanofibers. (a) Pristine K^{+}-doped RF nanofibers, (b) After ion exchange with Co salt solution, (c) After ion exchange with Ni salt solution.

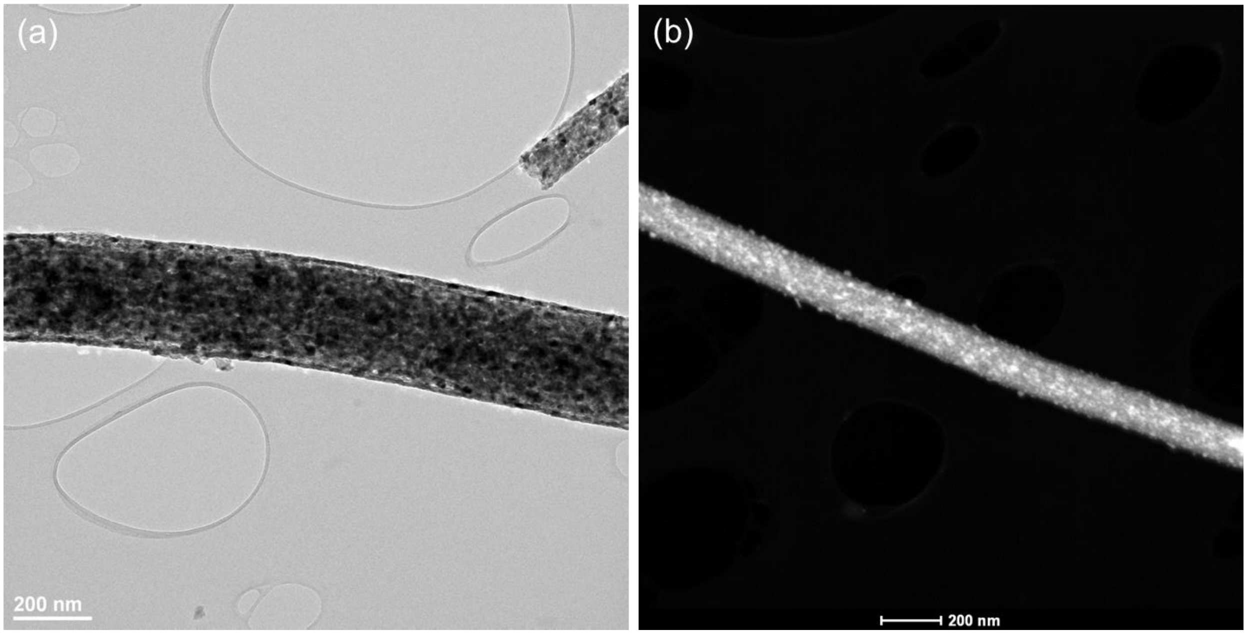

Figure 5 High resolution transmission electron micrographs of Co-doped carbon nanofibers. (a) Bright field HR-TEM image, (b) Bark field STEM image.

DISCUSSION:

In this project, we developed a novel ultraporous graphitic carbon nanofiber material using a synthesis strategy combining electrospinning and catalytic graphitization. In order to realize catalytic graphitization for creating graphitic nanostructures within the carbon fiber framework, we used a strategy that allows homogeneous distribution of transition metal particles throughout the carbon matrix. Resorcinol-formaldehyde (RF) gel was chosen as the carbon precursor because RF gel is well known to produce nanometer sized carbon particles via sol-gel reactions. When resorcinol (R) reacts with formaldehyde (F), RF hydrogels are synthesized via polycondensation, cluster formation, and gelation. Although direct mixing of RF gel with desired transition metal salts has been used to produce graphitic carbon materials, homogeneous distribution of the metal ions throughout the carbon precursor is not ideal.[5, 6] Here we adapted a strategy using a resorcinol derivative which contains inherent metal-binding sites.[7] Since each repeating unit of the polymer contains an ion exchange moiety, a much more uniform distribution of the metal dopants throughout the framework is ensured. Various transition metal salts (Fe, Co, Ni, Cu, Zr) can be exchanged and introduced into the carbon framework, which was used as an *in-situ* transition metal catalyst doped carbon precursor.

Electrospinning can readily produce amorphous carbon nanofibers, which subsequently can be fully graphitized at temperatures > 2000 ˚C to form densified carbon fiber.[8] With the introduction of transition metal particles into the carbon precursors, the electrospun carbon precursor fibers can be converted to graphitic carbon fibers by *in-situ* catalytic graphitization at a much lower temperatures (~1000˚C).[9, 10] Within individual carbon nanofiber frameworks are nanometer-sized graphitic structures consisting of concentrically layered graphene shells resembling fullerene (bulkyballs) structures. High curvature radii generally lead to high strain in the local structures, which are expected to lead to increased graphitic interlayer spacing.[11] The degree of graphitization and porosity will be studied as a function of transition metal catalysts, and thermal annealing conditions. The distance between adjacent graphene layers can be further tuned through selective oxidation and reduction.[12]

There were some challenges in the carbon precursor fiber fabrication by electrospinning. Adjusting the electrospinning operating conditions such as voltage and flow rate, and changing the polymer concentration by adding PVP, were unsuccessful improving the beading issues on fibers. After adding the non-ionic surfactant Triton X-100 to the source solution, with the solution electrospun in the same operating condition, it was observed that the beaded carbon fibers were dramatically reduced, and uniform electrospun fibers could be produced. This is because addition of surfactant to the solution could affect the formation of “Taylor Cone” during the electrospinning, which makes the electrospinning process much more stable.

We characterized the carbon fibers as synthesized by SEM, EDS, HR-TEM, and demonstrated the success incorporation of the transition metal catalysts. We also compared this ion-exchange method with directly mixing the metal catalysts with RF gel approach, and we found the metal particles distributed much more homogeneously throughout. When the high temperature furnace is up running for the project, we predict that fullerenic nano-onion structures will form within the carbon fiber framework by the homogenously embedded transition metal catalysts. As the graphitic carbon fibers are developed, we will conduct HR-TEM in conjunction with electron diffraction to quantify interlayer-spacing, crystallite alignments, and local structural ordering. Due to the epxected highly disordered nature of the proposed carbon materials, we will evaluate short-range order variations from the radial distribution functions computed from electron diffraction patterns.[13]

ANTICIPATED IMPACT:

The preliminary success achieved in this project provides a clear development path for fabricating scalable graphitic carbon materials required for electrochemistry study of multivalent rechargeable batteries. It leverages with another Exploratory LDRD (SAND2014-19745R, LDRD176606: Can Nanoporous-Carbon Host Materials Enable Multivalent Ion Electrochemical Energy Storage?), which successfully demonstrated that such a carbon host material does exist for Mg^{2+} intercalation, however with materials mass production restrictions. Because what is being proposed in the current project is using a scalable approach to produce graphitic carbon materials which contain large and potentially tunable interlayer spacing, it provides a practical solution of multivalent-ion intercalation into graphitic networks. These scientific progresses open the possibility of developing advanced energy-storage concepts and moving "Beyond Li". Enabling energy-storage systems that expand chemistry options to span a range of gravimetric/volumetric, energy/power densities, and lifetimes can help meet future energy security missions.

The success design of graphitic carbon with enlarged interlayer spacing will enable the MV-ion intercalation for the development of MV rechargeable batteries. Successful MV battery technologies will lead to higher energy density, lower cost, and better safety and reliability to meet the power demands. It directly ties to the DOE mission for “clean energy transformation”. It could also expand storage chemistry options to meet the nation’s energy security needs. This effort is in line with the goals of EERE/OVT, and supports DOE’s directives on electrical energy storage. It could also potentially attract widespread interest such as in nuclear waste cleanup, environmental remediation, and on-chip micropower for remote sensors, autonomous microelectronics, and extreme environments.

This work will be of interest to the larger scientific community due to the scalability of producing graphitic carbon materials with tunable interlayer spacing on the angstrom scale. We will use the relationships with JCESR and EFRCs to broadcast our success, and seek strategic collaborations. We will continue to seek follow up funding, for example, a follow-on FY16 Exploratory LDRD, and DS&A for the micro-battery developments, and JCESR for the high energy rechargeable battery development. IP creation will enable WFO/CRADA opportunities.

CONCLUSION:

We demonstrated a novel graphitic carbon materials synthesis approach which has scalable and economical production capabilities. We chose RF hydrogel as carbon precursors using a resorcinol derivative which contains inherent metal-binding sites on each polymer unit. Transition metal ions were successfully introduced into the carbon matrix by binding to the carboxylate groups through an ion exchange process. The transition metal species are used as *in-situ* catalysts to produce graphitic fullerene-like nanostructures surrounding them. A suitable and effective carbon intercalation material for MV batteries will position the intercalation anode in a very competitive position to impact and advance the energy storage research. The success design of graphitic carbons with enlarged interlayer spacing will directly enable the multivalent ion intercalation for the development of multivalent rechargeable batteries.

SPECIAL NOTE: The current SAND report summarized the work conducted in less than 2 months after starting the project. Due to a situation that the PI needs to take on a special assignment, it was not possible to complete all the milestones. Following the LDRD office instruction, we closed this project in its current form with a total spending of $35K. We are planning to submit a new proposal to finish up this work in FY16.

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