Molecular Dynamics Simulation Of Electrodes For Capacitors Made With Nano-Onions

Jordan A. Caraballo Vega, Frances Martínez Miranda Department of Mathematics Petra Mercado Bougart HS and University of Puerto Rico at Humacao, 100 Tejas Avenue Humacao Puerto Rico 00791

Faculty Adviser: Jose Sotero Esteva

Abstract

Supercapacitors are electrical devices composed by two electrodes and a dielectric material. They have the high storage capacity of batteries and the fast charging characteristic of capacitors. An approach to make such devices smaller while preserving the capacity to hold significant amounts of charge depends on the use of materials for electrodes that provide a large surface area for the adsorption of electrolytes. This work develops a model for molecular dynamics simulations of carbon nano-onions and tests how well electrodes made by agglomerating such structures increase the effective surface area on which electrolytes adsorb. Nano-onions are modeled using a few layers of fullerenes. The internal layers serve to give the molecule more realistic mechanical and geometrical properties. Molecular dynamics simulations of nano-onions with outer shells made of: C_{720} , C_{500} , C_{320} , C_{240} , C_{180} , C_{80} , and C_{20} fullerenes in water in order to observe the adsorption of electrolytes onto the nano-onions. Electrolytes were added and positive or negative charges were assigned to the carbon atoms in the nano-onions. The amount of ions adsorbed onto the onions was counted as a measure of effective area. It was found that nano-onions had enough binding energy to stay bundled in plain water as well as in the presence of electrolytes. The effective adsorption area is greater than in a plane electrode. Ions easily penetrate crevices and holes.

Keywords: Molecular dynamics, Electrodes, Nano-onions

1 Introduction

In order to conceive our world new ways to obtain the necessary energy to function, having in mind the conservation of renewable resources and safe processes. There have been increased interest different types of devices to conserve the available sources without diminishing their importance and uses. Technology has emerge rapidly through this recent years and with it devices that consume energy. It is expected that in 2017 the market of energy and storage systems such as batteries and supercapacitors will grow up to \$8 billion¹. Supercapacitors have been proposed as promising energy devices thanks to their high power density, recycle ability, and environmentally friendly characteristics ^[1-2-3]. They have the storage capacity of batteries and the fast charging characteristics of capacitors⁴. A factor that makes these devices different from other capacitors is the materials used as electrodes, such as carbon in different forms⁵. One approach to make such devices smaller while preserving their capacity to keep high amounts of energy consists of developing materials used as electrodes that increase the surface area. Porous materials based on carbon, such as activated carbon and agglomerates of carbon allotrope have been attractive materials to be used as electrodes due to their electrical energy storage characteristics, high conductivity, and accessible surface area for ion adsorption ^[6-7]. Increasing the surface area of the electrodes can be the responsible of producing a better adsorption of the

electrolyte.

This work studies surface area and ion adsorption characteristics of carbon nano-onions (CNO) agglomerates that could be useful when used as supercapacitor electrodes. Molecular dynamics simulations (MDS) were used to model the porous carbon electrodes of a regular arrangement of CNO. This is a technique which consists in computing the positions and velocities of the atoms interacting in a molecule from a determined initial state as time progresses in discrete time steps. The simulation was set-up using the Wolffia program and NAMD to carry out the simulations.

Term	Definition
CMD	Classical Molecular Dynamics
GUI	Graphical User Interface
NAMD	A molecular dynamics package for CMD simulations by the <i>Theoretical and</i> <i>Computational Biophysics</i> <i>Group</i> of the University of Illinois at Urbana Champaign.
VDW	Van der Waals radius.
VMD	Visual Molecular Dynamics, a molecular graphics software.

Table 1 glossary of terms used in this paper.

Term	Definition
PDB	Protein data bank, usually referring to a file format containing atom coordinates.
CNT	Carbon Nanotube.
NPT	Simulation model where the number of atoms, pressure, and temperature are constant
CNO	Carbon nano-onion.

2 Background

Supercapacitors are devices characterized by their rapid charging/ discharging ability, a high storage capacity as in batteries, and long cycle life. These devices are composed of two electrodes and a dielectric material working through the simple- charge separation mechanism between the two electrodes and the electrolyte⁵ (Figure 1). They accumulate charges at the electrode- electrolyte interface. With the obtainment of a higher surface area and high electrolytes concentrations capacitance values will increase⁵. These electrical devices have been used in load cranes, forklifts, large scale transport systems, and others. Porous carbon materials are being used as electrodes because of their high conductivity and high surface area. During the charging process, cations and anions in the electrolytes are attracted to the cathode and the anode to form electrical double layers in the pores of the electrodes.



Figure 1. Representation of a typical capacitor. The collectors are usually made of metal. Active layers of a carbonbased porous material is in contact with the collectors. The electrolyte separator permeable to the electrolyte is often made with polymers.

2.1 Nano-Onions

Carbon nano-onions (CNO), also called onion-like carbon or multi-shell fullerenes, are spherical conformations of graphitic carbon. CNO owe their name because of their multi-layer conformation seeming like the layers of the onions. This material has many attractive properties for energy storage, such as high conductivity, high surface area, and exceptionally fast charge- discharge rates⁸. Methods for the productions of these porous materials have been the electrode beam irradiation, condensation of carbon vapor, and vacuum annealing of nanodiamonds⁹. These materials have been studied for the use in electrical double layer supercapacitors because of their high surface area and porosity which helps through the adsorption of the electrolytes.

2.2 Molecular Dynamics

Classical molecular dynamics simulation is a technique that models and produces the positions and velocities of the atoms in a molecule from a determined time in Δt increments. This technique is used in investigations related to Physics, Chemistry, Biology, and other sciences seeking to be the most approximate to reality. The initial state is the known coordinates (positions x, y, z) and velocities of the atoms. The positions represent the localization of the center of each atom modeled as "soft" balls in a tridimensional space. The initial velocities depend on the simulated temperature of the system (1)

$$T = \frac{1}{NK} \sum_{i=0}^{N} m_i v_i^2.$$
(1)

Passing the Δt time the position and velocities of the atoms are calculated based in the force each atom exert to the other particles in the molecule. The computation of this force is based in formulas that model the potential energy (U) which formula is: $U = U(r_{ij}) = U_{LI}(r_{ij})+U_{bond}(r_{ij})+U_{angle}(r_{ij})+U_{torsion}(r_{ij})+U_{electric}(r_{ij})$. This force is the vectorial sum of all the forces. The Lennard Jones potential (2) indicates the attraction/repulsion act between non-bonded atoms. σ_{ij} represents the distance in which the particles can be located without making their electric clouds attract or repel. Force is obtained from potential

$$U_{lj}(r_{ij}) = 4\varepsilon_{LJ} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right].$$
(2)

To obtain the acceleration, velocity and new position the classical Newton laws are used (3):

$$a_{i+1} = \frac{F}{m}$$
, $v_{i+1} = a_{i+1}\Delta t + v_i$, and $r = v_i\Delta t + r_i$. (3)

2.3 Wolffia

Wolffia is an open source program with a graphical user interface (GUI) to set up, execute, monitor, and analyze Classical Molecular Dynamics simulations. A tab-based design intended to guide the user throughout the simulation processes simplifying the steps of mounting an entire molecular system. Steps such as selecting the molecules and setting force field parameter values are simpler with Wolffia thanks to their catalog of molecules and solvent, plus the force field editor. These parameters are fundamental in MD simulations. Once the system is built, the processes of potential minimization and MD simulations are executed with NAMD by pressing a button. The minimization process is the responsible of relaxing each molecule in order to find a stable point to start the simulations. With the Wolffia GUI using NAMD parameters like temperature, pressure, Mash Ewald options, and time can be controlled. Plots of temperature, potential, kinetics, and others are shown during the processes giving the user a clue of what is happening and strengthening the obtained results. Woffia can be found at http://wolffia.uprh.edu.

3 Methods

This section describes the process used to construct the CNO electrode- electrolyte model. First spherical CNOs were built and agglomerates of fullerenes are tested. Then an estimate of the increase in exposed surface area of a CNO packing compared to a planar region is performed. Finally a simulation of the movement of ions is made to determine adsorption pattern and the mobility of the ions through inter CNO spaces.

3.1 Fullerenes In Water

The coordinates files of 2,408 fullerenes were acquired from the Yoshida's fullerenes library. A custom bash and python code was written in order to convert all the files to a PDB format usable by Wolffia. Force fields values used are taken from CNT model. Simulations were performed with the purpose of testing this fullerenes CMD model by comparing the results with known behavior. In particular, individual fullerenes were simulated to observe their actual shape. Also fullerene aggregates in water were simulated in order to see if they dissolve. In that case, either the fullerenes are not good material for the electrodes or the CMD force field is not appropriate. Both sets of simulations were made controlling the temperature at 300 K using NAMD's Nose-Hover temperature control and the pressure was controlled at 1 atmosphere using Langevin control. This is also called a NPT ensemble.

Simulation of individual fullerenes quickly evolved from a nearly perfect spherical shape described in the fullerene library to a faceted shape consistent with their known shapes Figure 2a. Also, a very stable conformation of the fullerenes agglomerates was formed (Figure 2b). The interaction was seen and when solvent was added the behavior of the fullerenes remained stable. Fullerenes agglomerates did not dissolve (Figure 2c).



Figure 2. Fullerenes simulated by Classical Molecular Dynamics. (a) Most of the fullerenes found in Yoshida's library have spherical or cylindrical shapes but acquire a faceted shape similar to experimental observations after a small simulation. This is evidence that the force fields used produce realistic results. (b) A simulation of an agglomerate of 60 C_{100} fullerenes in vacuum remains stable. (c) The agglomerate remains stable when water is added to the system.

3.2 Nano-Onions

Observations found in literature of some CNOs show fairly spherical shapes instead of the polytope-like shapes of individual fullerenes described in section 3.1. Twenty combinations of fullerenes were tested with the purpose of producing a model of a CNO consisting of seven layers of fullerenes of decreasing size that preserve a nearly spherical shape throughout the simulation. The same simulation parameters used in section 3 were used to simulate the CNO in water. Figure 3a shows various shapes obtained. Combinations of fullerenes which deformed to faceted or abnormal shapes after a small simulation were discarded. The combination of fullerenes grouped in multi-layers demonstrated no deformation and good stability (Figure 3b). Fullerenes of sizes: C_{720} , C_{500} , C_{320} , C_{240} , C_{180} , C_{80} , and C_{20} are grouped in multi-layers forming the porous CNO.



Figure 3. Nano-onion models using fullerenes layers. (a) Examples of deformations from the desired spherical shape that appeared for different combinations of fullerenes. (b) The nano-onion selected for the next phase of this work whitout any significant deformation is composed by 7 layers of fullerenes: C₇₂₀, C₅₀₀, C₃₂₀, C₂₄₀, C₁₈₀, C₈₀, and C₂₀.

3.3 Packed Nano-Onions

Random aggregates of identical spheres would form a mass with crevices and holes that have the effect of a porous material. The effective surface area depends on the size of the molecules that should be adsorbed onto the surface and the size of the crevices and holes. An optimal sphere packing produces the tightest aggregates of spheres and, therefore, has less effective surface area than other arrangements. For the purpose of increasing effective surface area, an optimal packing is a pessimist assumption. The optimal sphere packing method was implemented with the intention of simulating a porous material made with CNO aggregates. This method consists in packing the spheres in a way which each sphere occupy the less surface possible creating a good area for the adsorption of the ions. This arrangement simplifies the estimation of the effective surface area.

An estimate of the effective surface area of the CNO optimal packing is done by subtracting the surface area of the regions were ions would not fit to the total surface area of the spheres. The area where the ions would not adsorb forms a spherical cap surrounding the contact point between the spheres. The computation of the spherical cap area (Figure 4) depends on the radius (r_s) of the outermost fullerene sphere of the nano-onion, the width of the ions in the mixture (e), and the Van der Waals radius (vdw) of the carbon atoms at the surface of the sphere. Since $h = \frac{e}{2}$ and the area of the spherical cap is given by $A_c = 2 \pi r h$, then $A_c = \pi r e$. In the packing used in this work each sphere is in contact with 8 other spheres. The total area of a sphere is $A_t = 4 \pi r^2$. Therefore, the exposed area per sphere is (4).

$$A_e = A_t - 8A_c = 4\pi r (r - 2e) \tag{4}$$



Figure 4. The area of a spherical cap at the contact point between spheres where ions cannot bind is the surface area that lies within the rectangular region (cylindrical in 3D) of width *e*.

As expected, the formula for A_e implies that, for a fixed sphere radius, the effective area per sphere depends on the size of the ions. For larger ions A_e could be in fact smaller than for an ordinary planar electrode. Suppose that the exposed area of the spheres at each layer is compared to the area of the planar region A_p that it replaces (Figure 5c). Then $A_p = (2r)^2 = 4r^2$. Taking into account the two layers the increase factor of the effective area (5) should be greater than one should the effective area of the packed CNOs be greater than the area of a planar electrode.

$$\frac{2A_e}{A_p} = \frac{8\pi r (r-2e)}{4r^2} = 2\pi \left(1 - \frac{2e}{r}\right)$$
(5)

As a consequence $2\pi \left(1 - \frac{2e}{r}\right) > 1$ which implies that (6)

$$e < \frac{r}{2}(1-\frac{1}{2\pi})$$
 (6)



Figure 5. Computation of the surface area where ions can be adsorbed. (a) The electrolyte is composed of sulfate and hydronium ions in water. Sulfate is the largest of them. Therefore sulfate ion is selected to calculate it size including its VDW radius. The sulfate atom is shown in yellow and the hydrogen atoms in red. (b) The widest part of the molecule is formed by the triangle formed by the sulfate atom and two oxygen atoms. This distance *c* is readily obtained using the cosine law. The width of the ion *e* is taken as *c* plus the VdW radius of the oxygen atoms. (c) The ion colud be adsorbed anywhere on a planar region A_p or on the region A_e if packed nano-onions are used.

A verification that, for the molecules used in this work, the effective surface area of the CNOs is larger than that of the planar electrode starts by estimating e and r. Being this a pessimist estimate of the effective surface area, the maximum width of sulfate is taken as e (Figure 5a and b). The cosines law formula was used for the measurements of the ions because of the form of the sulfate ion. Sulfate ions were selected because are larger than the hydronium ions. The length of the sides of the triangle that the sulfate ions form is the bond length b=1.43A and the angle that they form $a=120^\circ$. As a result, the size of the sulfate ion is c=2.48 Å without taking into account the VDW radius of the atoms. The VDW radius of the oxygen atoms, 2.2 Å, is then added to find the total width of the ion: e = 5.62 Å. The estimate of the maximum width of the nano-onions, being nearly spherical, is easily computed resulting in

r = 29.158 Å.

With the obtained values e = 5.62 Å and r = 29.158 Å the inequality (6) is readily verified: 5.62 < 12.257. The increase factor of the effective area for these values is greater than 3.8. Adding more layers would increase this factor.

3.4 Electrode

Rectangular periodic boundary conditions are used as shown in Figure 6a. These conditions are set to simulate an infinite space by repeating the same piece of a system to reduce the time required to simulate a large model. The width and depth of the box were set to match the dimensions of a layer of 9 optimally packed CNOs to simulate electrodes that extend infinitely in the directions of the *x* and *y* axes. The



Figure 6. Construction of the electrodes. (a) Two layers of nine nano-onions are arranged in an optimal packing as the base cell for the periodic boundary conditions. The periodic boundary conditions are set in a way in which overflowing spheres at one side of the box are matched with appropriate voids on the opposite face. (b) Solvent and electrolyte added to fill the box a densities corresponding with pressure 1 atm. and a temperature 298K. (c) Spheres are hidden to show how fluid is distributed. Representations of systems with black background were rendered using the VMD software.

simulations of the electrode can be done once the electrode is produced and the solvent and the electrolyte are added.

Initial simulations were performed using a concentration of electrolytes found in literature¹¹. Since the electrode in this simulation has nearly 4 times the surface area of a planar electrode, this concentration was then increased by a factor of 4. Therefore, since the initial quantity of solvent was 2362 molecules of sulfuric acid per box corresponding to 1575 ions of hydronium and 787 of sulfate because hydronium oxidation number is +1 and sulfate -2. After the increase electrolytes quantities increased to 6300 ions of hydronium and 3150 of sulfate for a total of 9450 molecules of sulfuric acid.

Initial simulations were performed using a concentration of electrolytes found in literature¹¹. Since the electrode in this simulation has nearly 4 times the surface area of a planar electrode, this concentration was then increased by a factor of 4. Therefore, since the initial quantity of solvent was 2362 molecules of sulfuric acid per box corresponding to 1575 ions of hydronium and 787 of sulfate because hydronium oxidation number is +1 and sulfate -2. After the increase electrolytes quantities increased to 6300 ions of hydronium and 3150 of sulfate for a total of 9450 molecules of sulfuric acid.



Figure 7. The system is equalized by simulation without applying charges to the electrodes (parameter q in yellow). Temperature and pressure plots show that the system stabilized.

A simulation of the system without applying charges to the electrodes and with the solvent added is performed to stabilize the pressure around 1 atmosphere using Nose-Hover option and letting the z component of the periodic box to vary. A temperature of 298 K using Langevin control and a time step size of 0.1 fs were applied to the simulations. Mesh Ewald options that consist in computing Coulomb forces for atoms that exceed the cutoff distance of MD simulations were applied as well. The coordinates of the CNO atoms

remained constant throughout all the simulations. Not fixing the CNO positions produce simulation in which electrodes are destroyed because they would contain loose molecules with equal charges that would repel. Temperature and pressure acquired stability as shown in Figure 7. Once pressures stabilized, simulated charges were applied to the electrodes. Fullerenes force fields parameters were edited with the purpose of increasing the speed of the simulations. Electrodes with atoms with charges +0.1 and -0.1 were simulated to observe how sulfuric acid ions adsorbed to the nano-onions. The simulation stabilized as well is the state was the system is ready to be simulated with charges applied.

4 Results and Discussion

When charges were applied to the electrodes ions were completely attracted to their respective electrode. The hydronium to the cathode, and sulfate to the anode (Figure 9a). Ions passed through the pores of the electrodes and were adsorbed within them (Figure 9b). The geometrical analysis presented in section 3.3 is sustained by these observations. The effective surface area includes part of the onions surfaces except for the spherical caps. To model the charge / discharge cycle charges were applied and then changed signs to observe how ions do went back to their respective charged electrode. During these simulations almost all ions were attracted to the respective electrode. Figure 9a shows the ion attracted to the nano-onions surface and Figure 9b the conformation of ions adsorbed to the electrodes. Images were created using the VMD program, Figure 9c illustrates the charge were all ions moved completely to their respective electrode filling the effective surface area and Figure 10a, b, and c show the electrode after implementing the discharge phase. There are presented the ions that did not go back to their respective electrode in Figure 10d. Just a few hydronium ions got trapped inside an electrode. The result implies that a capacitor based on this material may show some, but not much, deterioration in performance supporting the hypothesis that CNOs electrodes will show the long cycle life characteristics from the capacitors.



Figure 8. A simulation with charges applied to the nano-onions was performed. (a) The electrolyte was adsorbed onto the electrodes. Orange molecules represent sulfate and red-white molecules hydronium. Water is present in the simulation but not shown. (c) Nano-onions are hidden from view. Close-up of the electrodes with adsorbed Hydronium (top) and sulfate (bottom).

In this model the CNO coordinates were constant throughout the simulation. It is unlikely that electrodes made only with loose CNO would maintain structural integrity when charges are applied. Still the observations presented here apply to porous carbon materials. Applicability to electrodes made with CNOs could be done in cases were a method is developed to keep them bound together. The development of a process to form bonds between the outer layers of the nano-onions could be an option. In any case this method would not reproduce the expansion that has been observed experimentally in capacitor electrodes made with porous carbon.

The model of electrolytes used here does not include the hydrogen bonds that form between water and ions when sulfuric acid dissolves in water. In order of account for this an adjustment to the value of the parameter e in section 3.3 would suffice to geometrical analysis.

In any of the two situations discussed here the presented computational model holds as an appropriate model for simulating the interaction between ions of different sizes and CNO agglomerations.



Figure 9. Positive and negative charges were interchanged with the purpose of testing the mobility of ions in and out the crevices. The initial state is the same as in Figure 8(a). (a) Final state after the charges were changed. (b) Final state with hidden nano-onions. (c) The final state when periodic boundary conditions in the x axis direction are applied. (d) Close-up showing that a few sulfate ions could not escape the electrode where they were in the initial state. Other ions and water are hidden from view.

The aim of the model presented here is to study the adsorption of electrolytes on surfaces made of porous carbon materials. In order to simulate a complete capacitor the electrodes must be structurally sound. A known method to achieve structural stability consists of forming thin films of mixtures of conducting polymers and carbon allotropes such as CNOs. The simulation of such system by means of Classical Molecular Dynamics would require the computational resources that cannot be performed in a reasonable amount of time using the computers used in this work. A complete capacitor also has a separator. The scale of the simulation required to simulate such system is out of the scope of this work for the same reasons mentioned before.

A final aspect to be considered is that there is a debate in literature about the precision of simulations of charged porous materials. Some researchers argue that a detailed simulation of the adsorption patterns requires the use of polarizable force fields. An attempt to quantify with a high level of precision the observations made here would probably require such specialized approaches.

5 Conclusions

A model for a thin planar electrode of a material made of carbon nano-onions was presented as well as estimates of increase rates of its surface area compared to a flat material. Nano-onions aggregates have the potential to be used to produce electrodes. The model could be used to study the behavior of electrodes made with other porous carbon materials. An optimal packing configuration would provide an effective surface area at least 3.8 times than that of a single flat plate when sulfuric acid is used as an electrolyte. A formula to estimate a lower bound for this rate based on an optimal sphere packing relates the increase factor with the radius of the nano-onions and the size of the electrolyte ions was derived. When simulated with sulfuric acid used as an electrolyte the ions moved freely through the holes and crevices of the simulated electrode when charges were applied. Few ions remained trapped between spheres. A capacitor built with this material may show some, but not much, deterioration in performance. Further simulations and calculations may quantify this phenomenon.

6 Future Work

Current work includes testing other electrolytes such as KOH and ionic liquids for the production of the

capacitor. A way of producing new fullerenes of larger size with the intention of increasing the width of the nano-onions may be attempted producing a simulation with CNOs with sizes closer to those used in experiments.

7 Acknowledgements

This work is being sponsored by UPRH-PENN Partnership for Research and Education in Materials (NSF-DMR-0934195), University of Puerto Rico at Humacao. The authors thank the comments and suggestions made by the faculty affiliated to the UPRH-Penn-PREM Program.

8 References

- 1. Jampani, Prashanth, A. Manivannan, and Prashant N. Kumta. "Advancing the supercapacitor materials and technology frontier for improving power quality." *The Electrochemical Society Interface* 19 (2010): 57-62.
- Ma, Chang, Yan Song, Jingli Shi, Dongqing Zhang, Xiaoling Zhai, Ming Zhong, Quangui Guo, and Lang Liu. "Preparation and one-step activation of microporous carbon nanofibers for use as supercapacitor electrodes." *Carbon* 51 (2013): 290-300.
- 3. Wang, Yan, Zhiqiang Shi, Yi Huang, Yanfeng Ma, Chengyang Wang, Mingming Chen, and Yongsheng Chen. "Supercapacitor devices based on graphene materials." *The Journal of Physical Chemistry C* 113, no. 30 (2009): 13103-13107.
- 4. Simon, Patrice, Yury Gogotsi, and Bruce Dunn. "Where Do Batteries End and Supercapacitors Begin?." *Science* 343, no. 6176 (2014): 1210-1211.
- 5. Plonska-Brzezinska, Marta E., and Luis Echegoyen. "Carbon nano-onions for supercapacitor electrodes: recent developments and applications." *J. Mater. Chem. A* 1, no. 44 (2013): 13703-13714.
- 6. Gao, Yang, Yun Shen Zhou, Min Qian, Xiang Nan He, Jody Redepenning, Paul Goodman, Hao Ming Li, Lan Jiang, and Yong Feng Lu. "Chemical activation of carbon nano-onions for high-rate supercapacitor electrodes." *Carbon* 51 (2013): 52-58.
- Han, Fu-Dong, Bin Yao, and Yu-Jun Bai. "Preparation of carbon nano-onions and their application as anode materials for rechargeable lithium-ion batteries." *The Journal of Physical Chemistry C* 115, no. 18 (2011): 8923-8927.
- Yury Gogotsi, Vadym Mochalin, McDonough, Patrice Simon, and Pierre'Louis Taberna. "Carbon Nano Onions: The Ultimate Carbon Black." Drexel University, *nano.drexel.edu/wp-content/NCDs/Carbon-Nano-Onion_NCD.pdf*.
- McDonough, John K., Andrey I. Frolov, Volker Presser, Junjie Niu, Christopher H. Miller, Teresa Ubieto, Maxim V. Fedorov, and Yury Gogotsi. "Influence of the structure of carbon onions on their electrochemical performance in supercapacitor electrodes." *Carbon* 50, no. 9 (2012): 3298-3309.
- 10. Yoshida, M. "VRML gallery of Fullerenes (1991)." *The database is available at http://www. jcrystal. com/steffenweber/gallery/Fullerenes/Fullerenes.html* 20.
- 11. Volfkovich, Yu M., A. A. Mikhailin, D. A. Bograchev, V. E. Sosenkin, and V. S. Bagotsky. "Studies of Supercapacitor Carbon Electrodes with High Pseudocapacitance".