Hydrogenated C60 as high-capacity stable anode materials for Li-ion batteries

Article - August 2019
DOI: 10.1021/acsaem.9b01040

CITATIONS 2
READS 52

8 authors, including:

Joseph Teprovich
California State University, Northridge
40 PUBLICATIONS 613 CITATIONS
SEE PROFILE

Patrick A Ward
Savannah River National Laboratory
16 PUBLICATIONS 276 CITATIONS
SEE PROFILE

Chengxi Huang
Virginia Commonwealth University
29 PUBLICATIONS 330 CITATIONS
SEE PROFILE

Jian Zhou
Xi'an Jiaotong University
85 PUBLICATIONS 2,482 CITATIONS
SEE PROFILE

Some of the authors of this publication are also working on these related projects:

Direct LiT Electrolysis for Fusion Energy View project

Google View project
Hydrogenated C₆₀ as High-Capacity Stable Anode Materials for Lithium Ion Batteries

Joseph A. Teprovich, Jr.*,† Jason A. Weeks,‡ Patrick A. Ward,§ Spencer C. Tinkey,§ Chengxi Huang,⊥ Jian Zhou,⊥ Ragaiy Zidan,∥ and Puru Jena*⊥⊥

Department of Chemistry and Biochemistry, California State University Northridge, Northridge, California 91330, United States
‡Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, United States
∥Savannah River National Laboratory, Aiken, South Carolina 29803, United States
⊥Department of Applied Physics and Institution of Energy and Microstructure, Nanjing University of Science and Technology, Nanjing, Jiangsu 210094, P. R. China
⊥⊥Department of Physics, Virginia Commonwealth University, Richmond, Virginia 23284, United States
§Center for Advancing Materials Performance from the Nanoscale, State Key Laboratory for Mechanical Behavior of Materials, Xi’an Jiaotong University, Xi’an 710049, P. R. China

ABSTRACT: There is a need to develop high-capacity and stable anode materials for the next generation of lithium ion batteries that will power consumer electronics and of automobiles of the future. This report describes a systematic experimental and theoretical evaluation of a series of hydrogenated fullerenes (C₆₀Hₓ) for use as high-capacity anodes in lithium ion batteries. It was discovered that there is an optimal number of hydrogen atoms that must be chemically bonded to C₆₀ to achieve reversible lithiation. Under the optimized conditions, C₆₀Hₓ was found to have a stable capacity of 588 mAh/g for over 600 cycles at a current density of 0.05 A/g. Extended cycling studies at higher current densities demonstrated that this material is stable for 2000 cycles. Theoretical modeling of this system determined that electronic structure changes due to hydrogenation is responsible for the favorable interaction of Li⁺ with C₆₀Hₓ. This study represents a unique methodology for increasing anode capacity and optimization of an anode’s electrochemical properties by controlling the hydrogen content of the active material.

KEYWORDS: fullerene, anode, hydrogen, lithium ion battery, intercalation, electrochemistry

INTRODUCTION

The increased power demands of advanced consumer electronics has led to the search for materials that can enable higher capacity, safer, and longer lasting lithium ion batteries (LIB). In order for the next generation of LIB to achieve these demands, there is a need to replace the graphite anode which has a theoretical capacity of 372 mAh/g based on one lithium ion stored per six carbon atoms (Li:6C) in the charged state. Additionally, the lithiation potential of graphite is close to the reduction potential of lithium, possibly leading to plating of lithium on the electrode. This could produce lithium dendrites that can puncture the polyethylene separator leading to a short circuit and fire in the battery. This has also led to the extensive investigation and commercialization of LIB with lithium titanate (LTO) as an anode. The lithiation of LTO occurs at much higher potentials than graphite (1.5 V vs Li⁺/Li), which eliminates the possibility of lithium dendrite formation. However, the LTO anode has a much lower capacity than graphite (175 mAh/g vs 372 mAh/g), and a full cell would operate at a much lower potential (~2.4 V vs ~3.7 V when paired with a cathode such as LiCoO₂).

Early research on C₆₀ demonstrated that it is a suitable host matrix for various alkali metals resulting in a superconducting phase (M₃C₆₀) with a critical temperature (Tc) greater than 100 K under certain conditions. This ability of C₆₀ to act as a robust host of alkali and alkaline earth ions promoted its investigation as an anode for lithium, sodium, potassium, and magnesium ion intercalation. However, pure C₆₀ is not suitable as an anode material in commonly used liquid electrolyte systems in metal ion batteries (i.e., LiPF₆ in ethylene carbonate:dimethyl carbonate). After the intercalation of the metal cation, the resulting MₓC₆₀ material becomes soluble in the polar organic electrolyte solution, resulting in the dissolution of the electrode with cycling. This has limited the...
use of pure C60 anodes with polymer-based electrolytes in solid-state cells to overcome the solubility issue of the MxC60 with varying degrees of success.12−17 Functional groups have also been attached to the C60 molecule (carboxyl, ester, and piperazine) through multistep synthetic methods and utilized as anodes.18 The ester-functionalized C60 showed the highest reversible capacity (861 mAh/g specific capacity with 60 wt % active material in the electrode) after 100 cycles with 0.1 C cycling rate. This behavior is attributed to the ability of ester groups (or carboxylate groups) to bind lithium ions, donate electrons to the C60 cage, and increase the lattice void space and specific surface area for lithium intercalation.

Recently the MxC60 class of materials have attracted great interest as hydrogen storage materials through the reversible formation of a metal intercalated fullerene (MxC60H,19−21). The presence of the intercalated alkali metal facilitates the reversible formation of covalent C–H bonds on the C60 at relatively low temperatures and pressures. In MxC60Hx, it has been experimentally and theoretically shown that the intercalated alkali metal dictates the sites at which the formation of the C–H bond will occur on the C60. Some experimental results suggest that complete hydrogenation of the C60, formation of C60H60, is possible for the Na6C60 system.22 These studies clearly demonstrated a strong link between the ability of C60 to reversibly chemisorb hydrogen and the stoichiometric ratio of the alkali metal. Intrigued by these findings, we investigated the opposite—how does the presence of chemisorbed hydrogen on the surface of C60 affect its ability to intercalate alkali metal ions as an anode material?

To date, there have been only two studies to evaluate the electrochemical intercalation of hydrogenated fullerenes (C60Hx or C70Hx). The first study, by Loutfy, reported that C60Hx performed similarly to pure C60 and that the electrode dissolved during cycling showed minimal reversible capacity.23 On the other hand, C70Hx showed some reversible intercalation of lithium with a capacity of ~600 mAh/g; however, only eight cycles were reported at a cycling rate with a constant current rate of 0.1 C until a voltage of 0.005 V followed by a constant voltage step (at 0.005 V) until 2% of the constant current value is reached. Recently, the reversible intercalation of sodium ions in C60Hx utilizing a poly(ethylene oxide) (PEO)-based polymer electrolyte was demonstrated in the solid state.24 In this study, only one hydrogenated fullerene, with an average of 39 hydrogen atoms chemically attached to C60, was evaluated. This material showed an initial capacity of 230 mAh/g with a 10% capacity retention after 20 cycles when operated at 60 °C. Also, it has been demonstrated that the presence of hydrogen on graphite significantly enhanced the lithiation capacity of the material.25 The hydrogen atoms were transferred to the graphite via mechanochemical milling with a rare earth hydride (YH3).

The enhancement in the capacity demonstrated by the graphite−YH3 composite anode was attributed to the formation of negatively charged sites on the graphite surface, resulting in a higher number of lithium atoms that can be stored per carbon atom (Li,C60H versus Li,C60 for a graphite electrode). The presence of hydrogen increased the capacity of the hydrogen containing anode composite to 720 mAh/g.

In this current work, we wanted to completely rule out the possible contribution of the yttrium metal (or its hydride) to the anode capacity of a carbon-based anode and utilize a model system in which the hydrogen content of the material can be controlled. To achieve this, a series of hydrogenated fullerenes (C60Hx) were prepared via heat and hydrogen overpressure with pure C60 powder in one step.26,27 This approach would allow one to fully examine the effect of hydrogen on the carbon surface without any possible effects from a metal hydride (i.e., YH3). To accomplish this, a systematic experimental and theoretical study of lithium ion intercalation into a series of hydrogenated fullerenes (C60Hx) was performed. The average number of hydrogen atoms (x) attached to C60 was varied from 0 to 26 (0 to 3.44 wt %). Through this study we determined that there is an optimal level of hydrogenation that will facilitate reversible lithiation for 2000 cycles at high rates of charge/discharge. This enhanced reversibility of lithium intercalation in C60Hx is due to the electronic structure changes, namely, the breaking of the surface C–C π-bonds, which induces active/negatively charged carbon sites, as described through theoretical calculations. The C60H18 is primarily studied as an example, which contains three active carbon sites where Li cations would adsorb, resulting in the observed voltage plateaus in the galvanostatic cycling study. Based on the capacity of the material at a cycling rate of 0.05 A/g (~0.1 C), ~16 Li atoms can be stored per C60Hx molecule, which is a significantly higher Li/C ratio than the theoretical capacity of graphite currently utilized in commercial lithium ion batteries (Li:6C for graphite versus Li:3.75C for C60Hx). This unique approach to enhancing the capacity of carbon-based anode materials can potentially lead to new high-capacity anodes that can be tailored for other alkali and alkaline earth metal batteries.

### EXPERIMENTAL SECTION

**Materials.** LiPF6 in ethylene carbonate (EC)-dimethyl carbonate (DMC) was purchased from Novolyte. C60 and NMP were purchased from Sigma-Aldrich. Acetylene black (AB) was purchased from Fisher. Poly(vinylidene fluoride) (PVdF) was purchased from MTI Corp. C60Hx Synthesis. The method for hydrogenating the C60 has been previously described.28 Briefly, the C60 was ground with a mortar and pestle for 5 min to expose more surface area for hydrogenation inside of an argon-filled glovebox. After grinding, the C60 turns from a shiny black color to a dull brown color. In a typical hydrogenation reaction, 400 mg of ground C60 was loaded into a sample holder of a Hyenergy PCT Pro 2000 (Sieves Apparatus) and charged with 100 bar of H2. A reservoir attached to the sample (175 mL) was also charged with 100 bar of H2. The sample was heated to 350 °C over the course of 90 min and then soaked at that temperature for 6−72 h. Immediately after completion of the hydrogenation, the sample was cooled to room temperature and stored inside of the glovebox until use. These sample conditions were utilized to minimize cage fragmentation during the hydrogenation process as previously reported.29−31

**Material Characterization.** XRD was performed on a PANalytical X’pert Pro with Cu Kα radiation, and the samples were protected with a Kapton film to minimize oxidation. SEM images were acquired using a Hitachi SU8200 Series Ultimate Cold Field Emission SEM with varying accelerating voltages and magnifications. Samples were prepared in an Ar-filled glovebox and contained in Ar-filled containers until transfer into the instrument. Air exposure during sample insertion was <5 s. Electrochemical testing was performed using a Bio-Logic VMP3 multichannel potentiostat.

**Cell Assembly and Testing.** A dry powder anode composite consisting of C60Hx:acetylene black (AB):poly(vinylidene fluoride) (PVdF) (8:1:1 weight ratio) was used in the initial screening tests. For the screening tests ~1−2 mg of the anode composite was pressed into a nickel foam current collector. No effect on the capacity was observed for this loading amount. Swagelok type cells were then assembled with the anode composite on Ni foam, glass fiber filter paper as separator, Li metal as the counter/reference electrode, and 19190 paper as separator, Li metal as the counter/reference electrode, and
All of the hydrogen-containing samples, except for the 72 h lithiation/delithiation cycle for each sample, are shown in Figure 1 during lithiation of the anode and allow for a full cell to operate at a higher voltage than one using an LTO anode paired with a cathode.

The electrochemical properties of the hydrogenated fullerenes were determined by preparing a composite anode with C$_{60}$H$_x$: acetylene black (AB), and poly(vinylidene fluoride) (PVdF). The anode composites were then pressed into a nickel foam disk. The nickel disk containing the anode composite, a separator (glass fiber filter paper), lithium metal, and 1.0 M LiPF$_6$ in EC:DMC (1:1 weight ratio) were assembled in a Swagelok-type cell for cycling and cyclic voltammetry studies. This allowed for the initial screening of the samples to understand what quantity of hydrogen is optimal for this type of application. The first galvanostatic lithiation/delithiation cycle for each sample is shown in Figure 1a. All of the hydrogen-containing samples, except for the 72 h sample, showed a higher capacity than pure C$_{60}$. Additionally, all of the samples showed that lithiation of the hydrogenated samples occurred at lower potentials than that of pure C$_{60}$. The lithiation potentials are higher than that of graphite but lower than lithium titanate (LTO). This is advantageous because it would minimize/eliminate the formation of lithium dendrites during lithiation of the anode and allow for a full cell to operate at a higher voltage than one using an LTO anode paired with a cathode.

The cycling data for the first 50 cycles of the C$_{60}$H$_x$ samples at a 0.05 A/g current density are shown in Figure 1b. The pure C$_{60}$ sample showed an initial capacity of 186 mAh/g; however, the sample showed no capacity on subsequent cycles due to its solubility in the organic electrolyte, as expected. All of the other samples that contained hydrogen exhibited a sustainable reversible capacity over the first 50 cycles. For each of the hydrogenated samples, there is an initial rise in the capacity followed by a plateau after ~20 cycles. The hydrogen content also played a factor in the reversible capacity of the anode material with the 48 h hydrogenated sample (~2.5 wt %). It showed the highest capacity retention after 50 cycles in this initial screening, and it was determined that this sample contained the optimal amount of chemically bound hydrogen for this type of application. This sample was selected for further characterization and will be the focus for the rest of the experimental and theoretical studies hereafter.

To obtain a consistent and uniform sample for further testing of the 48 h sample, a slurry of this material with NMP was prepared by using the same weight ratio of C$_{60}$H$_x$:AB:PVdF (8:1:1) and cast as a uniform film on a Cu foil current collector. The initial capacity of the slurrycast on Cu foil has a much lower capacity than what was observed for initial screening test where the dry powder was compressed.
282 into Ni foam. We attribute this to the coating and shielding of
283 the active material (C_{60}H) by the added conducting carbon
284 and PVdF from the electrolyte solution during the slurry
285 formation. The slurry allowed for an improved cycling
286 performance over multiple cycles relative to the nonslurry
287 samples shown in Figure 1. As Figure 2a shows, there is a
288 gradual rise in the capacity as a function of cycle number over
289 the first 300 cycles up to 588 mA/g, and this capacity holds
290 steady for the next 300 cycles. After 500 cycles we examined
291 the effect of different current densities (0.1, 0.2, 0.5, and 1.0 A/g
292 between 0.005 and 3.000 V vs lithium. Inset shows the average capacity as a function of current density. (b) Galvanostatic
293 delithiation profile for selected cycles from the extended cycling study at 0.05 A/g.

Figure 2. (a) Capacity vs cycle number for a C_{60}H (48 h) anode on a
294 Cu current collector. The current densities are listed for the cycles. Cycling was performed at a current density of 0.05, 0.1, 0.2, 0.5, and
295 1.0 A/g between 0.005 and 3.000 V vs lithium. Inset shows the average capacity as a function of current density. (b) Galvanostatic
296 delithiation profile for selected cycles from the extended cycling study at 0.05 A/g.

This behavior was also consistent with the cyclic voltammetry
297 experiments (Figures S7–S12).

The gradual rise in the capacity and change in voltage profile
298 with cycling has been previously observed in other anode
299 systems such as hierarchical porous carbons (HPC), porous
300 carbon nanofiber webs, and nitrogen-doped carbon@graphene
301 nanosheets. All of these high-capacity anodes demonstrate a
302 significant increase in capacity as a function of cycling and is
303 attributed to activation of the electrode. This increase in
304 capacity is >150% of the original capacity for some of the
305 materials with this activation process occurring over hundreds
306 of lithiation/delithiation cycles. This same behavior observed
307 during the cycling of C_{60}H is attributed to the activation of
308 the electrode via pulverization of the electrode, resulting in the
309 exposure of more surface of the active material to the
310 electrolyte resulting in the increased capacity up to the steady
311 state. The lithiation of C_{60}H also causes a slight increase in the
312 crystalline lattice, which also opens more pathways for lithium
313 diffusion and active sites for the lithium ion to attach to the
314 molecule. Once the electrode reaches a steady state (after 315 ~250 cycles), a stable cycling capacity of the anode is
316 observed. This is consistent with SEM and EIS (Figures S13–
317 S18) analysis of the electrode during and after cycling. The
318 pulverization and increase in porosity of the electrode before 319 and after cycling are apparent in the SEM. In the precycled
320 electrode on the Cu foil, the surface of the electrode is rough
321 with high porosity while there is the formation of a compact
322 layer deeper within the electrode with a very low porosity. This
323 is attributed to the slurry casting method used and uniform
324 distribution of the PVdF binder throughout the electrode when
325 compared to the dry method utilized for the screening of the
326 materials with the Ni foam current collector (Figure 1). This
327 compact and low-porosity section below the surface of the
328 electrode is inaccessible to lithium ion intercalation, resulting
329 in the initial low capacity of the material. SEM imaging of the
330 cycled electrode on Cu foil clearly shows the formation of a
331 porous structure throughout the entire depth of the electrode. 332 As the pulverization and activation process of the electrode
333 takes place, the section once inaccessible to lithium ion 334 intercalation is now accessible, resulting in the increase in
335 capacity over the first 250 cycles (Figure 2).

The EIS data clearly show a reduction in the SEI surface
336 layer resistance, the charge transfer resistance, and double-layer
337 capacitance from the first cycle until the 800th cycle. This is 338 attributed to the pulverization of the electrode with continued
339 cycling with exposes more of the active surface to the
340 electrolyte which results in the increasing capacity with cycle 341 number. This is consistent with the SEM images with shows a
342 reduction in particle size and increase in connectivity of the 343 electrode with cycling. This is likely due to the expansion and
344 contraction of the electrode upon lithiation/delithiation, 345 respectively. Qualitative analysis of the EIS data derived from
346 an equivalent circuit model of the system showed nearly a 2
347 order increase in the Warburg impedance component from the
348 initial state to the 1000th cycle. Because the Warburg
349 impedance continually increases throughout cycling, this
350 insinuates that the gravimetric capacity of the material should
351 increase as well. We also observed a gradual decrease in the
352 overall resistance of the cell with cycling up to the 800th cycle. 353 This conductivity increase can be attributed to the activation of
354 our material and in turn will lead to lower overpotentials and
355 higher efficiencies in the cell, making it easier for effective
356 lithium uptake. However, after 1000 cycles we start to see an
357
increase in electrochemical resistance; this insinuates the potential decomposition of our material after prolonged cycling which is reflected in the gradual decrease in capacity after the 1000th cycle (Figure S19).

Ex situ XRD was also performed on the sample in the initial, lithiated, and delithiated states (Figure S20). The XRD pattern of initial state of the electrode (C_{60}H_{2-AB-PVdF}) was consistent with the pure C_{60}H_{2} sample. After the first lithiation of the electrode, the sharp diffraction peaks of the C_{60}H_{2} become broader and less intense, indicating a relatively amorphous product results. After the delithiation of the electrode, the diffraction patterns associated with C_{60}H_{2} reappear with some peak broadening, which indicate the C_{60}H_{2} is losing its crystallinity with increasing cycles. This finding is also consistent with the activation process of the electrode with cycling as determined by SEM, EIS, and galvanostatic cycling. Next, we examined the cycle stability up to 2000 cycles for rates of 0.1 and 0.5 A/g (0.2 and 1 C, respectively) after 50 conditioning cycles at 0.05 A/g (0.1 C).

Even at high current density, the C_{60}H_{2} (48 h) anode showed good cycle stability and capacity over this extended cycling study (Figure S19). When the cycling was switched to 0.1 A/g there is a gradual rise in capacity up 550 mAh/g. This is consistent with the steady-state capacity of a cell that wasycled at 0.1 A/g. After the 2000 cycles, the capacity of the anode still remains above 200 mAh/g at the high 0.5 A/g current density.

The ability to reversibly store Li within the fullerene matrix is not surprising based on prior work, which indicated that a Li_{x}C_{60} system exhibits superionic conductivity. Further NMR of Li and Na intercalated C_{60} also supported the idea that alkali metals can be mobile within the structure even in the presence of high hydrogen content. The ability to reversibly store Li within the fullerene matrix is a difficult task as there are numerous possible adsorption sites of Li atoms. On the basis of our previous results on C_{60}H_{18} and C_{60}H_{18}Li_{n}, we chose the initial configurations of C_{60}H_{2}Li_{n} by following the following guidelines: (i) The geometry of the nth candidate is based on the optimal configuration of C_{60}H_{2}Li_{n-1}. (ii) Li atoms should adsorb close to the active sites (if it exists) on the molecular surface. (iii) Li atoms should reside away from H atoms because of electrostatic repulsion. (iv) The usual possible adsorption sites of Li atoms on C_{60}H_{2} are on top of the pentagon center, the hexagon center, C=C bridge, and C-sites. For each value of n we have considered at least 10 possible adsorption sites for Li.

![Figure 3. Hole density isosurface of LUMO for pure (a) C_{60}, (b) C_{60}H_{2}, and (c) C_{60}H_{2}. (d) Schematic diagram for enhancement of Li adsorption by hydrogenation.](image)

The binding characteristics of Li changes as the hydrogen content of C_{60}H_{2} increases. For example, the binding energy of Li in C_{60}H_{2}Li is 1.57 eV, which is nearly the same as that in C_{60}Li (1.58 eV). This is because the Li atom prefers to adsorb on a pentagon-center-top site far away from the adsorbed hydrogen site as no negatively charged center is observed in C_{60}H_{2} (Figure 3c). These results indicate that a negatively charged center, induced by hydrogenation, is crucial for the stronger binding of Li on C_{60}H_{2}.

Next, we focused on the Li adsorption on C_{60}H_{18} and compared that to results on pure C_{60}. This is because C_{60}H_{18} (3.5 wt % H) was optimal for lithiation capacity according to our experimental results, and the geometry of C_{60}H_{18} has been previously well-established. We took the initial geometries of C_{60} and C_{60}H_{18} from the literature and fully relaxed them. We present the computed geometry of C_{60}H_{18} in Figure 4. To determine the optimal configurations of C_{60}Li_{n} and C_{60}H_{18}Li_{n}, it is a difficult task as there are numerous possible adsorption sites of Li atoms. On the basis of our previous results on C_{60}H_{18}Li_{n} and C_{60}H_{18}Li_{n}, we chose the initial configurations of C_{60}H_{18}Li_{n} by following the following guidelines: (i) The geometry of the nth candidate is based on the optimal configuration of C_{60}H_{18}Li_{n-1}. (ii) Li atoms should adsorb close to the active sites (if it exists) on the molecular surface. (iii) Li atoms should reside away from H atoms because of electrostatic repulsion. (iv) The usual possible adsorption sites of Li atoms on C_{60}H_{2} are on top of the pentagon center, the hexagon center, C=C bridge, and C-sites. For each value of n we have considered at least 10 possible adsorption sites for Li.

Our calculations show that Li atoms prefer to adsorb on top of the pentagon center on pure C_{60} and distribute uniformly on its surface. This is consistent with previous studies. The binding energy of each Li atom [defined as E_{b}(n) = E(C_{60}Li_{n-1}) + E(isolated Li atom) − E(C_{60}Li_{n})] gradually decreases with the number of Li atoms up to n = 18. Three stages are observed in the binding energy profile, namely, the average binding energies of the first six, second six, and third six are 1.73, 1.37, and 0.99 eV, respectively. Interestingly, these three stages of binding energy can also be deduced from the electronic energy levels of conduction states near the Fermi level, where, for instance, the 3-fold LUMO state corresponds to the bonding between Li-s and C-p orbitals (see Figure 3d).
to the first stage because each Li atom adds one valence
electron, and the adsorption of six Li atoms fulfills the LUMO
state. The large gap between electronic energy levels is the
reason for sharp increase in $E_b$. It is known that original C$_{60}$ has
a lithiation capacity of $\sim$12 Li per C$_{60}$, suggesting that the third
stage with a binding energy of 0.99 eV is a cutoff for Li
adsorption.
Next, we explore the case of C$_{60}$H$_{18}$, where very different
behavior of Li adsorption is observed. We found that the Li
atoms favor to adsorb around three specific C-sites instead of
uniformly distributing over C$_{60}$ (Figure 4). This is because
hydrogenation breaks the $\pi$-bonds and induces active sites/
negative charge centers on the surface, which bind strongly to
Li atoms. This can be confirmed by the hole density of LUMO,
which shows three isolated C-sites (marked by orange) with
localized charges, similar to the C$_{60}$H case. Consequently, Li
atoms are expected to bind more strongly with C$_{60}$H$_{18}$ than
C$_{60}$. We calculated the binding energy of each Li atom on
C$_{60}$H$_{18}$ using the formula $E_b(n) = E(C_{60}H_{18}Li_{n-1}) + E(\text{isolated}$
Li atom) $- E(C_{60}H_{18}Li_n)$. The binding energy profiles of Li
atoms on C$_{60}$ and C$_{60}$H$_{18}$ have different trend. For $n < 13$, the
binding energy of Li on pure C$_{60}$ is larger than that on C$_{60}$H$_{18}$. Reverse is the case when $n > 13$. For example, the calculated
binding energy of the first Li atom on C$_{60}$H$_{18}$, namely 1.07 eV, is
smaller than that on C$_{60}$ (1.58 eV). This can be explained by
the fact that the HOMO–LUMO gap of C$_{60}$H$_{18}$ (2.29 eV) is
larger than that of C$_{60}$ (1.64 eV). From the electronic energy
levels of conduction states around the Fermi energy, we also
find three stages separated by large energy gaps (>0.4 eV) for $n$
ranging from 1 to 16 (Figure 5). These are $n = 1–6$ (1.25 eV), $n = 7–12$ (1.17 eV), and $n = 13–16$ (1.12 eV), corresponding to the three voltage plateaus ($\sim$1.00, 0.65, and 0.25 V), observed experimentally. The average binding energies of first
and second stages are smaller than those of C$_{60}$ while that of the
third stage (1.12 eV) is larger than that of C$_{60}$ (0.99 eV),
suggesting that C$_{60}$H$_{18}$ can adsorb more Li atoms than C$_{60}$. When $n > 16$, $E_b$ becomes small (<0.9 eV). These results

Figure 4. Top and side views of atomic structure for C$_{60}$H$_{18}$, hole density isosurface of LUMO for C$_{60}$H$_{18}$ and optimal structures for C$_{60}$H$_{18}$Li$_6$, C$_{60}$H$_{18}$Li$_{12}$, and C$_{60}$H$_{18}$Li$_{16}$. Green, gray, and pink balls represent C, H, and Li atoms, respectively. Orange balls represent active C-sites.

Figure 5. Binding energy of each Li ion on C$_{60}$ and C$_{60}$H$_{18}$ as a function of number of Li ions (left). Energy levels near the Fermi energy for C$_{60}$, C$_{60}$Li$_{12}$, C$_{60}$H$_{18}$, C$_{60}$H$_{18}$Li$_6$, C$_{60}$H$_{18}$Li$_{12}$, and C$_{60}$H$_{18}$Li$_{16}$ (right). Orange and black lines represent occupied and unoccupied states, respectively.
explain the improved lithiation capacity (∼16 Li per C_{60}H_{18}).

On the basis of the above analysis, we conclude that the key to enhancing the lithiation capacity of C_{60}H_{18} is breaking of the C–C π-bonds, which induces active sites/negative charge centers on the surface. When x is small, the electrostatic repulsion between hydrogen atoms is small, and an even number of hydrogen atoms can adsorb on the neighboring C-sites, forming strong covalent bonds and stabilizing the surface. At intermediate hydrogen content, e.g., x = 18, the electrostatic repulsion between hydrogen atoms becomes strong enough to separate the adsorption sites of hydrogen atoms. In this case, the C–C π-bonds are broken by hydrogenation and active/ negatively charged C-sites appear on the surface. When x becomes even larger, the surface of C_{60} is mostly covered with hydrogen atoms, and the repulsion between hydrogen atoms and Li atoms becomes rather strong. This makes the adsorption of Li atoms more difficult. For instance, the binding energy of the first Li atom on C_{60}H_{26} is as small as 0.78 eV. This finding is consistent with the low capacity observed experimentally for the highly hydrogenated 72 h sample, which has an average hydrogen content of C_{60}H_{18} and a capacity of only 135 mAh/g after 50 cycles. Therefore, a moderate value of x is preferable for improving the lithiation capacity of C_{60}H_{x}.

CONCLUSION

We have demonstrated that the addition of chemically bound hydrogen can be used to manipulate the physical and electronic properties of C_{60}, allowing it to be used as a highcapacity anode for reversible lithium ion intercalation. It was determined that a sample containing ∼2.5 wt % H (∼C_{60}H_{18}) was optimal for this application. The chemisorbed hydrogen creates three negatively charged active sites on the C_{60} for lithium to adsorb and cause an expansion and pulverization of the electrode material. This process allows for the flow of lithium ions during galvanostatic cycling. By fine-tuning the amount of chemisorbed hydrogen on the anode material, we can effectively optimize this and similar materials to serve as ubiquitous hosts of various alkali and alkaline earth metals. We are currently investigating the ability of this class of materials for the intercalation of other nonvalent (Na^+, K^+) and divalent (Mg^{2+}) cations and will be reported in due course.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsaem.9b01040.

Additional experimental characterization: XRD, LDI-TOF-MS, galvanostatic charge/discharge, CV, EIS, and SEM (PDF)

AUTHOR INFORMATION

Corresponding Authors

*(J.A.T.) E-mail: joseph.teprovich@csun.edu.

*(P.J.) E-mail: pjena@vcu.edu.

ORCID

Joseph A. Teprovich, Jr.: 0000-0002-7285-4844

Chengxi Huang: 0000-0003-1491-3954

Jian Zhou: 0000-0002-2606-4833

Puru Jena: 0000-0002-2316-859X

Author Contributions

J.A.T., R.Z., and P.J. conceived, guided, and directed the experimental and computational work. J.A.W., P.A.W., and S.C.T. performed the experimental characterization. C.H. and J.Z. performed the theoretical calculations. The manuscript was written with input and contributions by all authors.

Funding

This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division, and the Savannah River National Laboratory LDRD program.

Notes

The authors declare no competing financial interest.

REFERENCES


