Anticipatory Life Cycle Assessment of Single Wall Carbon Nanotube Anode Lithium ion Batteries

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Executive Summary

Introduction – There is a critical need for life cycle assessment (LCA) during the formative stages of technology development, so that the systemic environmental consequences of new technologies may be identified and mitigated early in product development cycles. For example, several studies have called for the application of LCA to nanotechnology. However, LCA typically relies on detailed inventory and performance data collected from *existing* industries at commercial scales. In the case of nanotechnology, collecting manufacturing and use-phase LCA inventory data is problematic, both because nanotechnologies are proprietary and because the energy and material flows studied at the laboratory-scale will likely change as the technology matures. This necessitates the development of *anticipatory* LCA methods that can be used to explore potential environmental impacts of developing nanotechnologies before they exist at scale.

Methods – Anticipatory LCA seeks to overcome the paucity of data through scenario development and thermodynamic bounding analyses. Critical components of anticipatory LCA include: 1) laboratory-scale inventory data collection for nano-manufacturing processes, and preliminary performance evaluation, 2) thermodynamic modeling of manufacturing processes and developing scenarios of efficiency gains informed by analogous material processing industries, and 3) use-phase bounding to report inventory data in a functional unit descriptive of performance. Together these analyses may call attention to environmentally problematic processes or nanotechnologies *before* significant investments in R&D and infrastructure contribute to technology lock in. The following case study applies these components of anticipatory LCA to single wall carbon nanotube (SWCNT) manufacturing processes, compares the rapid improvements in SWCNT manufacturing to historic reductions in the embodied energy of aluminum, and discusses the use of SWCNTs as free-standing anodes in advanced lithium ion batteries.

Case Study – SWCNTs can be synthesized through at least four different pathways: chemical vapor deposition (CVD), high pressure carbon monoxide (HiPCO), arc discharge, and laser vaporization. HiPCO demonstrates comparatively lower environmental burdens because it is a continuous flow process with recycled exhaust gasses, and thus has potential for scale-up to produce kilogram quantities of SWCNT. We model the degree of perfection (a second law measure of efficiency) of the HiPCO process, and develop scenarios for future improvements which

represent improvements in critical process parameters. Finally, we convert the energy requirements of each scenario into a functional unit of kWh battery storage capacity in a bounding-type analysis based upon existing measurements and theoretical limits. Assuming complementary advances in cathode technology and optimized battery geometry, SWCNT-enabled lithium ion batteries might store between 1.44 and 3.96 Wh / gSWCNT. Combining the outputs of the thermodynamic model with these two limiting-case conversion factors provides a range of energy requirements per kWh storage capacity.

Results and Conclusion – If the energy requirements of SWCNT manufacturing do not decrease, SWCNT anode batteries will require between 60 MWh of electricity per kWh storage capacity in the battery (the battery performs at its theoretical limit) and 160 MWh / kWh storage capacity (low performance battery). These values represent the energy requirements for SWCNT-anode manufacturing alone, and do not account for the remainder of battery manufacturing processes. This is more than two orders of magnitude greater than existing lithium ion battery manufacturing processes. Thus, research improving the *functionality* of SWCNT anodes alone is unlikely to result in an environmentally viable technology. However, research efforts focused on decreasing the energy intensity of SWCNT manufacturing processes may result in technologies with practical potential to generate environmental benefits. The most ambitious scenario of manufacturing efficiency gains yields values near .8 MWh per kWh storage capacity. Our results suggest that improving the yield of SWCNT relative to CO_as C input (called the synthesis reaction yield) is the most promising pathway for environmental improvements in the HiPCO process. The process SRY may be increased through recycling of exhaust gasses and further optimization of catalyst-feedstock interaction. Thus, anticipatory LCA may suggest alternative research agenda that may contribute to the development of more environmentally beneficial nanotechnologies.

Introduction

Until recently, the environmental impacts of developing technologies were neither explored nor regulated until after commercialization. (One exception may be recent environmental assessments of ethanol and biofuel production, see for example Rogers and Seager (2009).) Thus, technological innovation has been disconnected from environmental assessment and regulation (Dewick, Green et al. 2004; von Gleich, Steinfeldt et al. 2008), which has positioned environmental governance as retrospective and reactive (Davies 2009). Nonetheless, there is a growing realization that environmental intervention at the nascent stages of technology development may be more effective. Therefore, there is a critical need to transcend retrospective models of environmental assessment and regulation by applying life cycle assessment (LCA) to technologies at these early stages (Fleischer and Grunwald 2008; Meyer, Curran et al. 2011), such that life cycle environmental tradeoffs can be explored in modeling scenarios before significant investments in infrastructure create technological lock-in or result in stranded costs.

I. Towards Anticipatory Life Cycle Assessment

LCA is increasingly recognized as the appropriate framework to understand the environmental impacts of processes, technologies, and industries (Curran 2004; Bauer, Buchgeister et al. 2008; Eason 2011) because it accounts for shifting of environmental burden from one life cycle phase to another (e.g., increased battery lifetime at the cost of increased energy investments in manufacturing). However, existing LCA methods are insufficient for developing technologies (Wiek, Lang et al. 2008; Meyer, Curran et al. 2009). Real-time assessment and governance of technology necessitates the development of novel *anticipatory* LCA methods that can be used to quantitatively explore environmental impact scenarios, and relate findings in a decision-oriented manner (Canis, Linkov et al. 2010; Linkov, Bates et al. 2011).

II. LCA of Novel Nanotechnologies

A suite of examples illustrate the need for, and challenges that impede, the development of anticipatory LCA methods for nano-enabled energy technologies. A number of experts, including the United States Environmental Protection Agency (USEPA) and Woodrow Wilson Institute for Scholars have called for the application of LCA to nanotechnology (Klopffer 2007; Savage 2008; Şengül, Theis et al. 2008; Theis, Bakshi et al. 2011). In practice, this is problematic for several reasons:

- Uncertainty regarding the human and ecological health impacts of nanomaterials (Oberdörster, Oberdörster et al. 2005; Wiesner, Lowry et al. 2006; Bell 2007; Oberdörster, Stone et al. 2007; Stefani, Paula et al. 2011; Wiesner and Bottero 2011),
- High variability between engineered nanomaterials with the same chemical composition (Landi, Ruf et al. 2005; Powers, Palazuelos et al. 2007),
- Uncertainty in extrapolating laboratory-scale inventory data to commercial scales (Seager and Linkov 2008; Gutowski 2010; Gutowski, Liow et al. 2010), and
- Selecting a use phase-relevant functional unit that captures the potential benefits of engineered nanomaterials (Wender and Seager 2011).

Because of these challenges there are, to date, no complete LCAs (e.g., cradle-to-cradle) of novel nano*products*, although cradle-to-gate analyses of nano*materials.* The ecotoxicity of specific nanomaterials is relatively the most studied (Gavankar, Suh et al. 2012), although Eckelman, Mauter et al. (2012) suggest that the environmental impact of manufacturing and upstream processes may outweigh downstream, direct exposure impacts. Thus, cradle-to-gate analyses of nanomaterials have called attention the energy intensity of nano-manufacturing processes (Healy, Dahlben et al. 2008; Khanna, Bakshi et al. 2008; Ganter, Seager et al. 2009; Anctil, Babbitt et al. 2011; Grubb and Bakshi 2011), but do not account for the potential benefits provided by nanomaterials in the use phase. Few LCAs have overcome use phase uncertainty in selecting a relevant functional unit – exceptions are Walser, Demou et al. (2011), Reijnders (2010), Lloyd and Lave (2003), yet these analyses do not incorporate recent human health and toxicology research (Plata, Hart et al. 2009). Finally, the environmental tradeoffs of end-of-life recycling and processing of nanomaterials (Olapiriyakul and Caudill 2008) are explored independent of research into exposure pathways (Benn and Westerhoff 2008; Köhler, Som et al. 2008; Maynard 2009), which in turn is uninformed by research into social and market acceptance of nano-enabled technologies (Scheufele, Corley et al. 2007; Siegrist, Cousin et al. 2007; Siegrist, Wiek et al. 2007). Table 1 organizes the existing science, and shows how the fragmented efforts that inform different aspects of nano-LCA have yet to be integrated in a comprehensive whole.

Table 1: Relation of Nanostructured Material and Product Research Needs to LCA

	LIFE-CYCLE STAGE			
	Acquisition	**Purification & Manufacture**	**Use**	**End-of-life Disposition**
Material abundance & acquisition	scarcity & criticality of materials [46]	by-product & waste minimization	risk assessment for emissions inventory & characterization, including source term characterization, fate & transport, exposure and dose-response assessment [39, 40, 50]	
Bioavailability & Toxicity				
Synthesis pathways	energy & material intensity [11, 25, 32-38, 45]			
Life-cycle characteristics		technology comparison [30, 31]	cost, functionality & efficiency [28, 29]	persistence, mobility, bioaccumulation [19-23]
Social context	geopolitical sensitivities	worker safety [49]	market acceptance [43, 44]	disposal & take-back regulations [41, 42]

More importantly, Table 1 suggests that anticipatory LCA requires knowledge from multiple fields of study. Different research questions and investigative methods are required at each life cycle stage, and LCA of nanotechnology cannot proceed without parallel research in prerequisite specialty areas. That is, anticipatory LCA must incorporate social science, materials science, environmental science, and sustainability science perspectives in order to be applicable across *all* of Table 1.

III. Scale, LCA, and Thermodynamic Limits

Anticipatory LCA confronts the problem of data scarcity through a combination of scenario development and thermodynamic analysis of manufacturing processes and technology performance. Specifically, by coupling laboratory-scale inventory data with simplified technology performance modeling and projecting returns to scale, it is possible to provide upper and lower boundaries on environmental indicators of interest (e.g., embodied energy) for a specific technology. Three critical methodological components of anticipatory LCA are:

1. Creating laboratory-scale material and energy inventories, and determination of the laboratory or pilot-scale thermodynamic degree of perfection. Those processes that are far from thermodynamic perfection might be expected to improve more quickly than those that are already approaching practical thermodynamic limitations (Gutowski 2010; Gutowski, Liow et al. 2010).
2. Analogous experience curve modeling. It is well understood that high technology industries improve cost, material and energetic efficiencies as total production knowledge accumulates. Analysis of experience curve patterns from more mature industries (e.g., aluminum) may result in estimates of efficiency gains that accrue as emerging technologies are scaled up (McDonald and Schrattenholzer 2001; Yu, van Sark et al. 2011).
3. Calculating upper and lower boundaries to use-phase performance based on theoretical limits and existing laboratory measurements (Wender and Seager 2011).

In situations of high uncertainty (e.g., nano-enabled energy technologies) this analysis can be used to develop scenarios of environmental burden, and may call attention to environmentally problematic processes and technologies. Furthermore, by providing estimates of manufacturing and use-phase efficiency respectively, these analyses can lead to prioritization of research needs that will lead to the most meaningful environmental improvements. For example, an environmental agenda might call attention to research needs in manufacturing, rather than in product use-phase performance. These analyses characterize developing products cradle-to-use, and model results are ultimately incorporated into existing LCA tools (e.g., Simapro and EIO databases) to broaden system boundaries and account for supply chain impacts, as shown in figure 1.

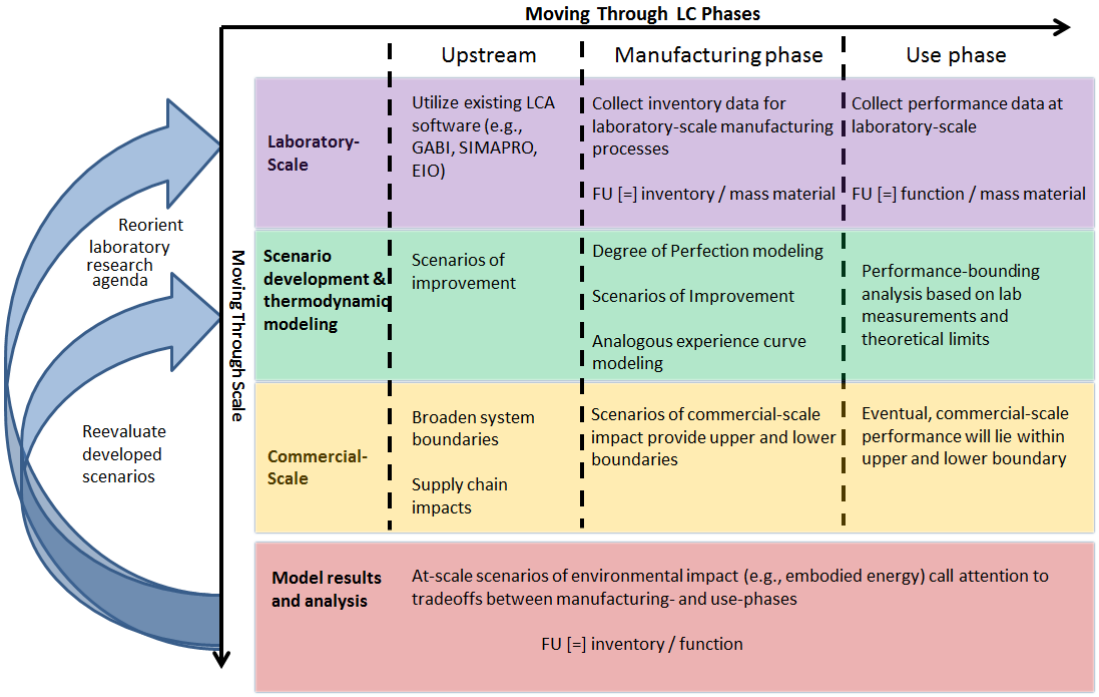

Figure 1: Cradle-to-use Components of Anticipatory LCA for Developing Nanotechnologies

The anticipatory LCA framework is iterative – initially a bounding-type analysis but moving towards forecasting LCA as data improve. Furthermore, the proposed cradle-to-use analyses described above may be expanded to include end of life impacts with further research (Schauerman, Ganter et al. 2012). More importantly, thermodynamic bounding analyses of technologies in their nascent stages may call attention to life cycle phases with the most potential for environmental improvement. Thus, anticipatory LCA may reorient a scientific research agenda towards pathways with decreased environmental burden. The following case study applies these components of anticipatory LCA to single wall carbon nanotube (SWCNT) manufacturing processes, compares the rapid improvements in SWCNT manufacturing to analogous material processing industries, and discusses the use of SWCNTs as an active anode material in advanced lithium ion batteries.

Case Study: Single Wall Carbon Nanotubes for Lithium ion Batteries

A major thrust of battery research is to increase the energy storage density of rechargeable batteries. This is motivated in part by consumer preference for lightweight electronics, but is increasingly important as electric and hybrid electric vehicles are implemented on larger scales. Recently, the energy density of batteries has increased by a factor of five—from lead acid batteries with a mass-based energy density up to 50 Wh/kg to lithium polymer

batteries approaching 250 Wh/kg. Lithium ion batteries have emerged as the preferred chemistry because of their comparatively high energy densities per unit mass (Wilburn 2008). Further improvements will depend upon increasingly sophisticated materials and manufacturing techniques, and engineered nanomaterials are appealing because of their large surface area and unique electrical properties. Specifically, single wall carbon nanotubes (SWCNTs) can store lithium ions, collect charge carriers, and conduct charge to external circuits (Landi, Ganter et al. 2008; Landi, Cress et al. 2011). SWCNT anodes may eliminate the need for charge collecting metal foil used in conventional lithium ion anodes, thus reducing battery weight and increasing energy storage density. The potential gains in use phase performance in SWCNT-enabled lithium ion batteries could justify increased energy investments in SWCNT manufacturing. However, there is no data available describing commercial scale manufacturing of SWCNT anodes, and only preliminary laboratory-scale data describing their use phase performance potential. Thus, the systemic environmental consequences of SWCNT-enabled lithium ion batteries are inherently unclear, and necessitate anticipatory LCA methods to quantitatively explore energy tradeoffs between the manufacturing and use phases. Specifically, the aforementioned analyses can provide insights into future developments in nano-manufacturing processes (e.g., potential sources of efficiency gains) coupled with comprehensive use-phase modeling (e.g., from present capabilities to thermodynamic limits) to evaluate the promise of future nanotechnologies from cradle-to-use. Ultimately, these results can be incorporated into existing LCA tools to broaden system boundaries and include potential supply chain impacts of future technologies.

I. SWCNT Manufacturing from an Environmental Perspective

SWCNTs can be synthesized through at least four different pathways: chemical vapor deposition (CVD), high pressure carbon monoxide (HiPCO), arc discharge, and laser vaporization. Early environmental assessments have called attention to the massive electricity consumption, high-purity input materials requirements, and low synthesis yields common to these processes (Healy, Dahlben et al. 2008; Ganter, Seager et al. 2009; Canis, Linkov et al. 2010). The majority of environmental impact is attributable to electricity consumption during SWCNT synthesis and to a lesser extent purification processes, while the most significant impact categories are climate change, airborne inorganics, and acidification. HiPCO demonstrates the comparatively lower environmental burdens because it is a continuous flow process with recycled exhaust gasses, and thus has potential for scale-up to produce kilogram quantities of SWCNT (Aditi, Helen et al. 2008).

II. Mechanisms of the HiPCO Process

The HiPCO process is a specialized form of chemical vapor deposition through which SWCNTs are produced at a high rate from a carbon monoxide (CO) feedstock (Nikolaev, Bronikowski et al. 1999; Richard E. Smalley 2004). Catalytic iron nanoparticles, formed *in situ* by the thermal decomposition of $Fe(CO)_5$ and aggregation of gas-phase Fe atoms, provide preferential sites for CO disproportionation, shown below in (1). The formation of solid carbon from CO gas in disproportionation, promotes formation of SWCNT on the surface of the catalyst via the *Yarmulke* mechanism (Hafner, Bronikowski et al. 1998; Moisala, Nasibulin et al. 2006). Briefly, a hemispherical carbon cap forms on appropriately sized particles, and the cap is pushed away from the catalytic particle by the addition of carbon atoms until the particle becomes too large and overcoats with amorphous carbon, or too small and evaporates (Bladh, Falk et al. 2000; Bronikowski, Willis et al. 2001).

$$2CO\ (g) \leftrightarrow CNT\ (s) + CO_2\ (g) \quad (1)$$

$$\Delta \quad 275.1\ [kJ/mol\text{-}CO] \quad 469.62\ [kJ/mol\text{-}C] \quad 19.87\ [kJ/mol\text{-}CO_2]$$

Listed below reaction (1) are the standard exergies of formation of the reactants and products. The exergy of formation represents the useful energy input to create the species from the environmental 'dead state', and is one component of a second law analysis of the HiPCO process. Second law analyses are preferred to first law analyses because the second law accounts for energy quality (i.e., how much useful work can be derived from it) as opposed to total quantity (Dewulf, Van Langenhove et al. 2008). Overall, the reaction releases 60.7 kJ/mol-C (or 5.06 kJ/g-SWCNT) at standard conditions (Szargut, Morris et al. 1988; Gutowski, Liow et al. 2010) and consequently is exothermic and spontaneous. However, the reaction rate is significant only at temp C (Renshaw, Roscoe et al. 1970) and increases with pressure, thus the HiPCO process requires -

C) and pressure (30-50 atm) conditions to drive the reaction forward. Reaching and maintaining these conditions (i.e., changing the physical exergy of the CO gas stream) requires exergy inputs, which when combined with the chemical exergy input in the form of CO, is currently orders of magnitude greater than energy released in disproportionation.

III. Degree of Perfection of the HiPCO Process

The degree of perfection provides a measure of the second law efficiency of manufacturing processes, and is defined as the ratio of the chemical exergy of the product(s) at standard conditions to the sum of all exergy input (Szargut

and Morris 1987). Assuming the kinetic and potential exergy of the CO gas stream is negligible, the degree of perfection can be estimated as,

(2)

where the standard chemical exergy of SWCNT ($b_{ch,\ SWCNT}$) is 469.62 kJ/mol-SWCNT, as shown in Reaction One. Assuming ideal gas behavior, the minimum physical exergy (b_{ph}

C, ~30 atm) is given by (3),

(Szargut, Morris et al. 1988).

(3)

The total input exergy is then given by the sum of physical inputs and the standard exergy of CO feedstock, then multiplied by the mole ratio of CO to SWCNT (given by the inverse of the synthesis reaction yield, SRY) to result in the total input exergy per mole of SWCNT produced. When the HiPCO process was first reported in 1999, inputs were greater than 600,000 grams of CO per gram of SWCNT (Nikolaev, Bronikowski et al. 1999), and by 2004 were on the order of tens of thousands of grams CO per gram SWCNT (Richard E. Smalley 2004). These historic improvements in the degree of perfection are shown in Figure 2

C and 30 atm, and three scenarios of process improvement into the near future.

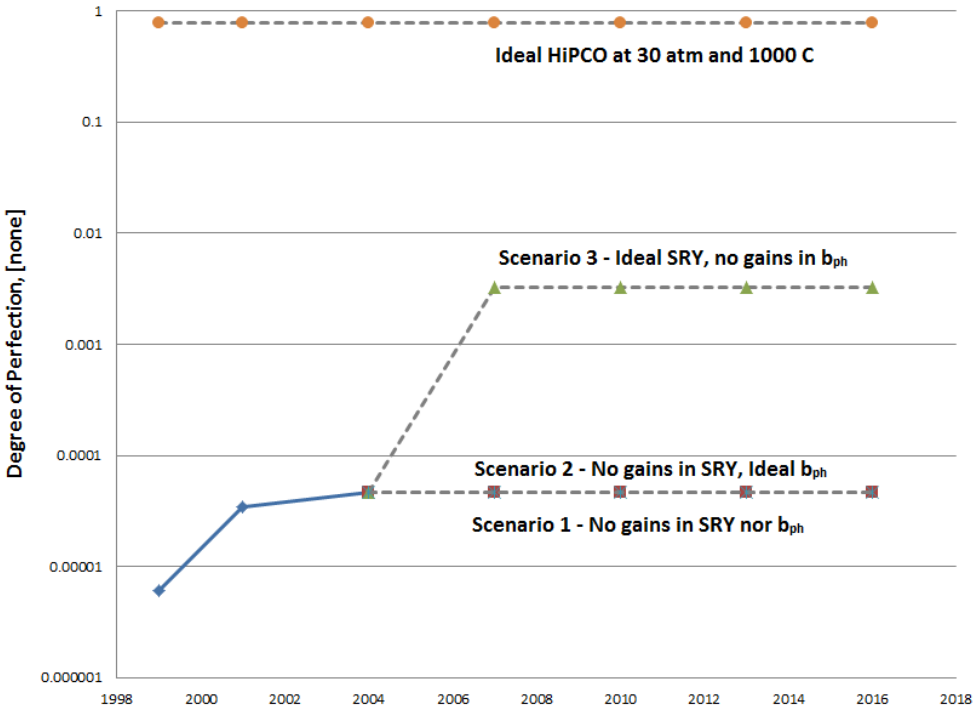

Figure 2: Historic Improvements in the Degree of Perfection of the HiPCO Process, and Three Scenarios of Future Improvement

Scenario One assumes no process improvement from values reported in the 2004 pattent, and thus provides the upper bound of manufacturing exergy requirements. Scenario Two represents ideal b_{ph}, but no improvements in SRY from 2004 values. It is noteworthy that, because the reported SRY values are on the order of 10^{-5}, reductions in b_{ph} do not result in improved DoP. Conversely, Scenario Three represents the stoichiometric ideal SRY, but assumes no reductions in b_{ph} from 2004 values. In this scenario, the DoP improves dramatically (despite fixed b_{ph}) because the SRY dominates process inefficiency at this point. The ideal (although never attainable) manufacturing process has a degree of perfection of unity, and smaller values indicate increased potential for efficiency gains. The degree of perfection for SWCNT manufacturing processes are on the order of 10^{-4} which indicates significant room for improvement. By comparison, electric induction melting processes have a degree of perfection on the order of 10^{-1} (~.7), and are thereby approaching their second law limit (Gutowski, Branham et al. 2009).

IV. Analogous Experience Curve Modeling

It is well understood that the thermodynamic and economic efficiency of material manufacturing processes improve with increased experience and scale. Similar to SWCNT manufacturing processes, at one time the energetic demands of aluminum processing were prohibitive of large scale production and application. Nonetheless, the discovery and scale-up of the Hall-Heroult electrolytic reduction process prompted significant reductions in the embodied energy of aluminum. Specifically, as the Hall-Heroult process matured (i.e., increased experience and increased in scale), the specific energy demands of aluminum production asymptotically decreased towards the theoretical minimum (Haupin 1986), as shown in Figure 3 (top). The rapid improvements in thermodynamic efficiency of the Hall-Heroult process are analogous to early improvements in SWCNT manufacturing via the HiPCO process. In the time between first reporting of the HiPCO process in 1999 and patenting in 2004, the thermal exergy (which is the sum of the physical and chemical exergy described above) required to produce an equivalent mass of SWCNT decreased by more than an order of magnitude, as shown in Figure 3 (bottom).

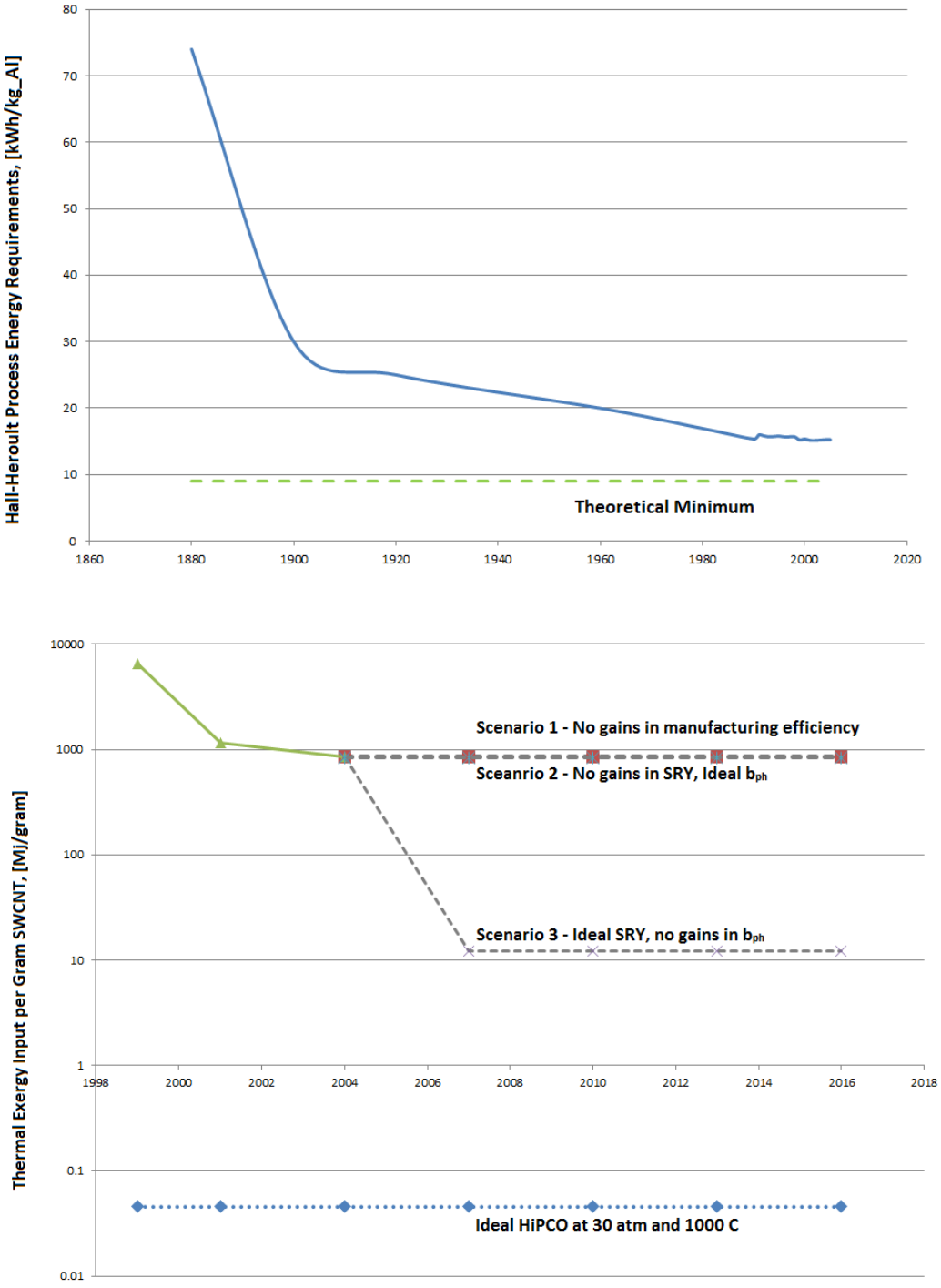

Figure 3: Historic Reductions in Aluminum Process Energy and Analogous Improvements in the HiPCO Process

The significant improvements assumed in Scenario Three are informed by inspection of historic thermodynamic experience curves. Furthermore, the rapid gains in manufacturing efficiency demonstrated by both processes illustrate the challenge of early environmental assessment of rapidly developing technologies – LCA is trying to hit a moving target. Nonetheless, there are several analogous historical examples of advances in material processing that enabled the development and growth of transformational industries. For example, improvements in aluminum processing enabled the aerospace industry and advances in silicon manufacturing enabled semiconductors and resulting information and communication technologies. By analogy, we can reason that sufficient improvements in SWCNT manufacturing efficiency may result in establishment of a new, nano-enabled, technology revolution. However, the next section will reveal that LCA of SWCNT processes as they exist now holds little potential for environmental benefits.

V. Use Phase Performance Bounding of SWCNT Anode Lithium ion Batteries

Half-cell testing of SWCNT anodes reveals a reversible capacity of 400 mAh / gSWCNT, compared to a theoretical limiting capacity of 1100 mAh / gSWCNT (Landi, Ganter et al. 2008; Landi, Cress et al. 2011). Both values represent a significant improvement over traditional lithium ion battery anodes (made of mesoporus carbon beads) which provide a reusable capacity around 150 mAh / gC. The specific energy density of the battery is computed as the product of specific capacity and cell voltage, nominally 3.6 volts for $LiCoO_2$-carbon battery cells (Linden 1984), which is a generous assumption as early research indicates decreased voltage profiles. Assuming complementary advances in cathode technology and optimized battery geometry, SWCNT anode lithium ion batteries might store between 1.44 and 3.96 Wh / gSWCNT. Using these two limiting cases to provide upper and lower boundaries on battery performance, the thermal exergy scenarios output by the model are presented in a functional unit representative of battery performance, specifically kWh storage capacity, as shown in Figure 4.

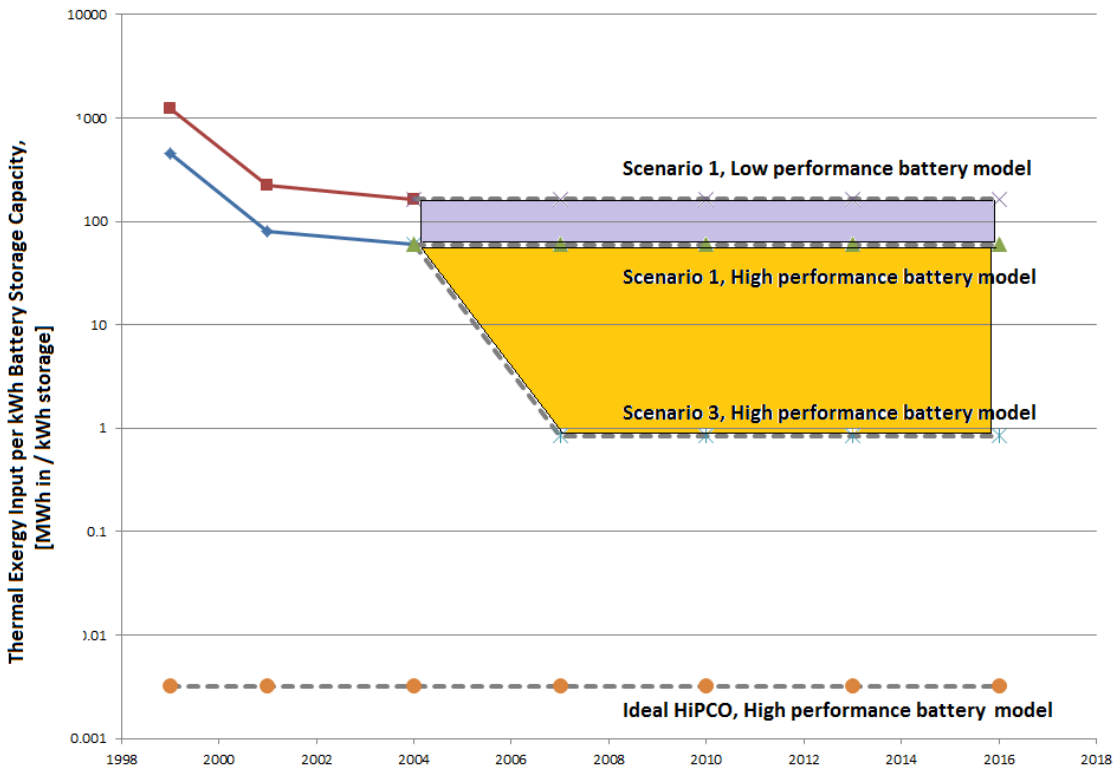

Figure 4: Thermal Exergy Requirements per kWh of Storage Capacity of SWCNT Anode Lithium ion Batteries, for SWCNT Synthesis via HiPCO According to Two Scenarios Discussed Above

The single line depicting historical thermal exergies splits into two – representing the high performance battery (lower line) and low performance battery (upper line). If no improvements in the manufacturing efficiency are realized, the eventual embodied exergy of SWCNT anodes will lie between 60 and 160 MWh / kWh storage capacity (the upper purple region). This represents the exergy to produce the anode alone, and does not account for the remainder of the battery manufacturing processes. The yellow shaded region indicates the range of likely values if the HiPCO increases material efficiency as described in Scenario Three.

VI. Discussion and New Directions

A recent LCA of conventional-carbon anode lithium ion batteries reports energy investments of .47 MWh per kWh storage capacity (Samaras and Meisterling 2008) – over two orders of magnitude less than SWCNT anodes alone. Thus, research improving the *functionality* of SWCNT anodes alone is unlikely to result in an environmentally viable technology. However, research efforts focused on decreasing the energy intensity of SWCNT manufacturing processes, may result in technologies with practical potential to generate environmental benefits. Thus, establishing

upper and lower boundaries to use phase performance and combining these limits with laboratory-scale manufacturing data can be used to quantitatively explore tradeoffs between improved technological performance associated with use of engineered nanomaterials and the significant energy investments inherent in nanoscale engineering.

One pathway to reduce the environmental burden of carbon nanotube manufacturing processes is to improve the synthesis reaction yield (SRY) of nanomanufacturing processes. Typical SRY values are less than five percent for three of the four established SWCNT synthesis pathways discussed above. However, a recent study of SRY in laser vaporization in batch processes demonstrated that use of nano-scale catalysts results in yields closer to 35% (Schauerman, Alvarenga et al. 2009). Further improvements in the life-cycle environmental performance of SWCNT manufacturing processes can likely be achieved through recycling of inert gasses and catalysts, as well continuous-flow process optimization, and returns to scale.

Conclusion

Research and development of nano-enabled energy technologies is inherently uncertain, and the tools necessary to conduct environmental assessment, specifically LCA, under such uncertainty have lagged behind nanotechnology development. Paradoxically, current approaches to LCA are least able to inform environmental understanding in the early stages of technology development when LCA could most reduce the eventual systemic environmental burdens of the technology. This necessitates the development of *anticipatory* LCA methods, which employ thermodynamic analysis as a guidepost for understanding both the limits of manufacturing improvements and use phases performance, thereby replacing a complete lack of data with potential scenarios. Ultimately, an anticipatory analysis can contribute to reorientation of laboratory research agenda towards pathways with decreased environmental burden. This chapter presented an example demonstrating the limits of a research agenda that focuses on improving use-phase performance of SWCNT-enabled lithium ion batteries alone as being less valuable than research into decreasing energy requirements of SWCNT manufacturing processes.

Supporting Information

The 'high pressure carbon monoxide' (HiPCO) process is a method for producing single wall carbon nanotubes (SWCNTs) via the disproportionation of carbon monoxide (CO), shown below in reaction 1 (Szargut and Morris 1987; Gutowski, Liow et al. 2010).

$$2CO\ (g) \leftrightarrow CNT\ (s) + CO_2\ (g) \qquad (1)$$

$$\Delta \qquad 275.1\ [kJ/mol\text{-}CO] \quad 469.62\ [kJ/mol\text{-}C] \quad 19.87\ [kJ/mol\text{-}CO_2]$$

C) and thus requires high pressures (≈30 atm) in order to drive the reaction forward. The operating conditions and critical parameters (e.g., reactant gas flow rate, product yield rate) of the HiPCO method, representing three distinct points in process development (Nikolaev, Bronikowski et al. 1999; Bronikowski, Willis et al. 2001; Richard E. Smalley 2004), are summarized below in table 1.

Table 1. Process Parameters and Data for SWCNT Formation via the HiPCO Process

Publication	CO Flow Rate [mol CO/sec]	SWCNT Yield Rate [mol CNT /sec]	CO/SWCNT mol ratio [mol CO / mol SWCNT]	CO/SWCNT ratio [g CO/g SWCNT]
Nikolaev et al, 1999	.0037	1.4×10^{-8}	270,000	630,000
Bronikowski et al, 2001	.21	4.5×10^{-6}	47,143	110,000
Smalley et al, 2004	.0074	2.0×10^{-7}	36,429	85,000
Ideal HiPCO	N/A	N/A	2	4.66

Assuming the kinetic and potential exergy flows are negligible, all exergy flows through the system are either physical exergy (b_{ph} – the exergy associated with changes of state) or chemical exergy (b_{ch} – the exergy contained in the material feedstocks). The minimum physical exergy required to reach operating conditions of an idealized HiPCO processes, consisting only of heating and pressurizing CO gas, is given by (Szargut, Morris et al. 1988)

— — —— (2)

Where P_0 is 1 atm, P is 30 atm, T_0 is 373 K, T is 1373 K, c_p for CO is assumed to a be constant 1.04 kJ/kg_CO K, and the specific gas constant for CO is .2968 kJ/kg_CO K. The chemical exergy carried in the reactants is given by the exergy of formation of CO (275.1 kJ/mol-CO as shown in equation 1 above) multiplied by the molar ratio of CO to SWCNT (called the synthesis reaction yield, SRY) (Healy, Dahlben et al. 2008). The sum of the physical and chemical exergy (called the thermal exergy, b_{th}) is used to calculate of the degree of perfection (DoP) of the HiPCO method, which provides a measure of processes' the second-law efficiency, and is given by

(3)

Where the chemical exergy of SWCNT is 469.62 kJ/mol_C as shown in equation 1 above. Historical improvements (1999 to 2004) in the DoP of SWCNT manufacturing via the HiPCO process are shown in figure 1 below, along with three scenarios of improvement (2004 – 2016) based on gains in either the SRY or reductions in b_{ph}.

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