Energy Engineering using Carbon Nanomaterials as Interfacial Modifiers

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ABSTRACT

Nanomaterials can change either the rates or energetics of physical or chemical processes that occur at, or depend upon an interfacial process. Minimal amounts are then required and their purpose and placement being well defined. Highlights of such applications are presented in the areas of catalysis, energy storage, thermal management, and tribology.

Keywords: catalysis, modifiers, nanofluids

1 INTRODUCTION

Energy engineering encompasses energy processes such as conversion, generation, storage, efficiency, conservation and control. Creating a new paradigm, nanomaterials, when used as interfacial modifiers have the potential to significantly alter the energy landscape, given that these processes occur predominantly at interfaces.

2 EXPERIMENTAL

Experimental details will be presented at the presentation with regards to the synthesis and utilization of the nanomaterials. Further details may be found in the cited references.

3 RESULTS AND DISCUSSION

Results illustrate the theme and support the hypothesis of using nanomaterials as interfacial modifiers to advance gains in energy engineering. Selected examples from the author's work include catalysis, energy storage, thermal management, and tribology.

3.1 Thermal Management

Gains in nanofluid thermal conductivity have been attributed to interfacial fluid ordering, long-range phonon transport and particle aggregation. Through comparisons between nascent and functionalized nanocarbons, interfacial (molecular) ordering was shown to be the major factor responsible for thermal conductivity enhancement. This is applicable for both elongated MWNTs and compact carbon black aggregates, whose structures are represented in figure 1.
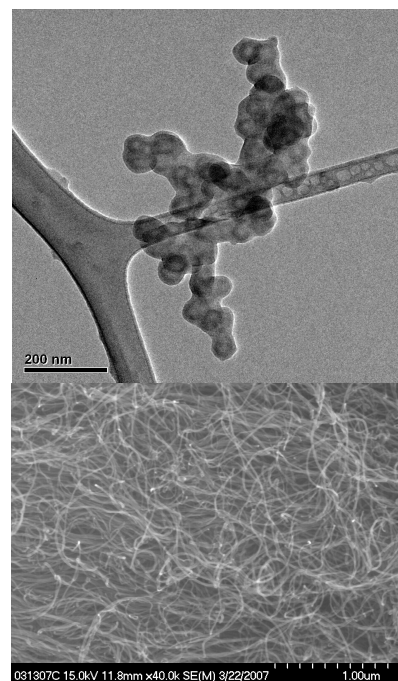
Figure 1 – Comparative HRTEM image of carbon nano-onions (CNOs) and SEM image of carbon nanotubes that have been tested for use in nanofluids. Increases of $\sim 20\%$ in base fluid (water) thermal conductivity were measured for ~ 0.25 wt.% addition [1].

Comparisons between graphitized and nongraphitized carbon black revealed a relatively small enhancement to nanofluid thermal conductivity knf by internal phonon transport. This applied for both functionalized and nonfunctionalized forms. The similar nanostructure of MWNTs and carbon black allowed comparisons between these two different nanocarbons with very different morphologies. Different morphologies permit surrogate testing of particle clustering while maintaining identical concentrations and dispersions. For the same concentration these two different nanocarbons exhibited nearly identical thermal conductivities. Although functionalized forms of each carbon had substantially higher nanofluid thermal conductivities than their nonfunctionalized (nascent)

counterpart forms, nearly identical values were observed for MWNTs and carbon black as additives at two different concentrations. This comparison between the two morphologies and different concentrations suggests an additional contribution to the thermal conductivity [1].

Dispersion of each material is important to achieving maximum enhancement for a given additive amount. Well before establishment of a percolation threshold, partial networks can form. Distinct from aggregation forming compact assemblies, clustering results in spatially distributed partial "networks" consisting of a few contacting nanoparticles. Functionalization may aid the formation of such networks through hydrogen bonding. Such interparticle connections eliminate fluid-nanoparticle junctions and associated resistances while establishing instead particle-particle connections. The phonon transport through these solid-solid connections is expected to be much more facile given matched phonon frequencies between the CNTs. As a result nanoadditive concentrations below the percolation threshold can offer substantial gains in thermal conductivity via this mechanism. Given that solid-state phonon transport as governed by nanoparticle nanostructure is not significant, the operative physical factor by which partial networking enhances thermal conductivity is reduction of interfacial resistance. Correspondingly higher concentrations are less effective as proportionally fewer nanoparticle-fluid interfaces are eliminated (in favor of more solid-solid connections). Establishment of extended networks (clusters), ultimately reaching a percolation network may impose a practical limit on the nanocarbon additive concentration given fluid viscosity constraints of practical cooling systems.

3.2 Tribology

While carbon nanotubes (CNTs) and carbon nano-onions (CNOs) have not enjoyed the commercialization that other carbon materials such as DLS and GLC, they possess distinct advantages that will eventually lead to commercialization. A major problem in this field has been the lack of inexpensive materials driven by the manner of synthesis and requirements of further purification for CNTs. The development of commercially feasible, inexpensive production scale processes for CNOs on the other hand are close to reality. A second problem with the development of applications is the differences between nanomaterials obtained by the different processes described by various researchers in the field, a problem which will be overcome by commercial production of these materials. In our efforts we have relied on numerous suppliers of MWNTs and SWNTs, and have developed the technology to produce large quantities of pure, high-quality CNOs, illustrated in Fig. 2. As gauged by friction coefficient and lifetime, the conditions for successful deployment of these nano-structured materials is highly dependent on the environment, the tribo-couples involved and the nanomaterials employed [2]. With proper choice of system,

it is possible to obtain ultra low friction and long wear life. These materials would then appear to be reasonable choices for graphite, one of the most widely used lubricants.
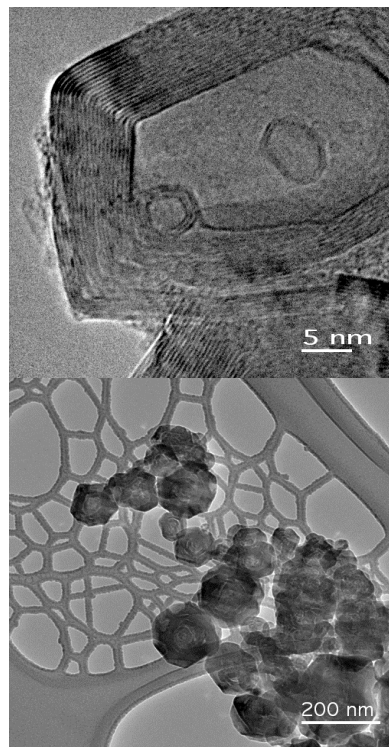

Figure 2 – High and low magnification images by TEM of the carbon nano-onions developed for tribology applications. The high degree of graphitic quality is evident in the top image.

3.3 Battery

The flame formed multi-wall carbon nanotubes and nanofibers were grown using four different catalysts (Ni, Cu, Co, and Fe) on two different substrates (Ni foil and Stainless steel mesh). The nanocarbon materials were examined using SEM and TEM, as illustrated in Fig. 3. The electrochemical properties of the nanocarbon to store-release lithium were also studied [3]. Experimental results indicated that the nanocarbon grown from a nickel foil substrate were graphite-like, but those grown from stainless steel mesh substrate were hard-carbon-like. Nickel catalysts produced carbon nanofibers that, when used as the anode material in lithium batteries, had a higher reversible capacity and higher irreversible capacity than the nanocarbon produced by other catalysts. All nanocarbons has defects that were responsible for the high irreversible capacity during the cycles of lithium insertion-release. The post-treatment of the nanotubes/nanofibers at 1000 ºC in nitrogen to remove surface oxygen and reduce bulk defects, followed by CVD carbon coating to reduce surface defects, was found to be best in reducing irreversible capacity and improving reversible capacity of the carbon nanotube. All

defects can be reduced by 1000ºC post-treatment in nitrogen and/or PVD carbon coating. The post-treatment of 1000ºC post-treatment in nitrogen followed by PVD carbon coating was found to be best in reducing irreversible capacity and improving reversible capacity of the nanocarbon, as Fig. 3 suggests. This is believed to be the results of bulk defect reduction and surface oxygen removal by the heat treatment, and the surface defect reduction by the amorphous carbon coating in vacuum.
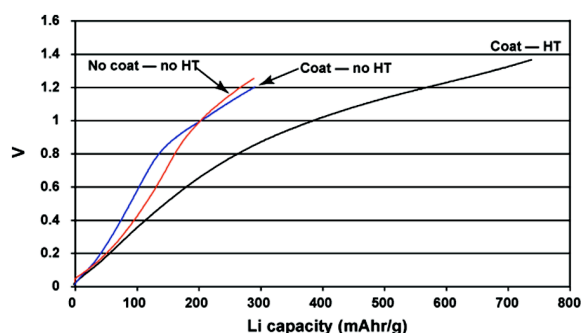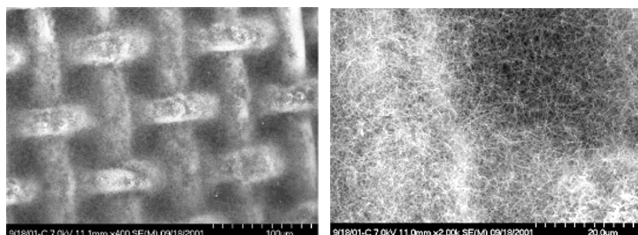

Figure 3 – Scanning Electron Micrograph (SEM) Images of Carbon Nanotubes (CNTs) Synthesized Directly Upon Stainless Steel (SS) Mesh. The lower plot shows that the CNT surfaces increases the Li ion capacity beyond the theoretical limit of normal graphite.

3.4 Catalyst

The activity enhancement in the CO hydrogenation by means of a ruthenium-supported carbon nanotubes on an open cell porous structure was compared for different catalyst preparations. Carbon nanotube supported ruthenium catalysts were prepared using three different synthesis protocols, and two different support systems were investigated as methanation catalysts. The metal/MWNTs were deposited over open-cell foam structures to create a hierarchical catalyst support structure with enhanced heat and mass transfer and low-pressure drop. Consequently, these nanostructured catalytic systems have the potential to significantly reduce the size of reactors, and enable localized control of thermal conditions to maximize conversion in equilibrium-limited processes.

TEM analysis of the ruthenium-decorated carbon nanotubes prepared by excess solution impregnation indicates the lowest surface coverage and average particle size of 1.3 nm. The micrographs of other three catalytic systems illustrated a superior decoration of active sites on the support with an average diameter size on the order of 2

nm. Depending on the synthesis protocol, ruthenium-deposited carbon nanotubes showed different methane yields. Values are summarized in Fig. 4.
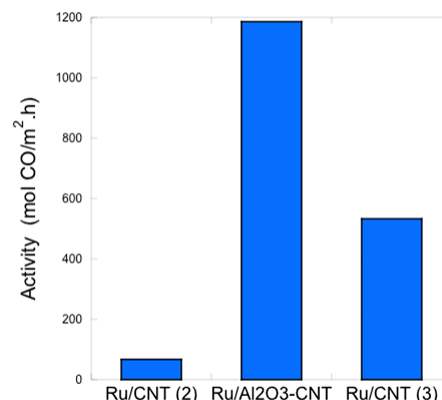
Figure 4 – Bar graph summarizing the activity of the Ru catalysts as prepared by different methods. Decoration of the CNTs by the Ni ion activation method produced the best results for the CNTs as support, but the mixed alumina-CNT support proved to be a superior system. The mixed support system enabled better CNT dispersion and aided catalyst accessibility by preventing CNT agglomeration.

Comparing the syntheses method, the do-decyl benzene sulfonate (DDBS) adsorption impregnation produced the highest activity level in the methanation process. CH4 selectivity is slightly lower. Nevertheless, a remarkable increase in the activity by a metal surface was observed when alumina nanopowder was added to a carbon nanotube support. This can be attributed to the superior dispersion of the CNTs with alumina nanopowder and better interaction between the ruthenium decorated nanosupports and the surface of the foams, producing a more homogenous nanostructured coating and a higher exposition of ruthenium nanoparticles on the nanostructured catalyst [4].

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