



## Open Archive TOULOUSE Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible.

This is an author-deposited version published in : <http://oatao.univ-toulouse.fr/>  
Eprints ID : 16747

**To link to this article** : DOI: 10.1016/j.carbon.2016.09.001  
URL : <http://dx.doi.org/10.1016/j.carbon.2016.09.001>

**To cite this version** : Nie, Chunyang and Galibert, Anne-Marie and Soula, Brigitte and Flahaut, Emmanuel and Sloan, Jeremy and Monthieux, Marc *A new insight on the mechanisms of filling closed carbon nanotubes with molten metal iodides.* (2016) Carbon, vol. 110. pp. 48-50. ISSN 0008-6223

Any correspondence concerning this service should be sent to the repository administrator: [staff-oatao@listes-diff.inp-toulouse.fr](mailto:staff-oatao@listes-diff.inp-toulouse.fr)

# A new insight on the mechanisms of filling closed carbon nanotubes with molten metal iodides

## ABSTRACT

Filling double-walled carbon nanotubes with iodine and various metal iodides (metals, alkali metals and transition metals) by the molten phase method was performed and the influence of possibly relevant chemical and physical properties of the filling materials on the filling rate was investigated. It was found, within the metal iodides series, that the filling rate can be mainly related to the redox potential ( $E_{\text{MIX/M}}$ ) of the filling material. Other parameters such as the possible formation of dimers, surface tension, or the early release of iodine may also play an additional role in the filling process.

Filling the inner cavity of carbon nanotubes (CNTs) with foreign materials is of great interest since the templating effect provided by their inner, elongated cavity gives rise to the formation of 1D materials with very narrow diameters and high aspect ratios [1], especially when single-walled carbon nanotubes (SWCNTs) or double-walled carbon nanotubes (DWCNTs) are considered. CNTs can be filled in different ways [1] and among them the molten phase method has been very popular for filling various types of CNTs due to the possibility for high filling rates, simplicity and versatility [2]. When metal halides, as well as iodine, were first attempted to be introduced into SWCNTs and DWCNTs by this method [2,3], it was surprisingly found that filling succeeded even when starting from closed CNTs, which revealed that the chemical activity of the halides toward polyaromatic carbon can be used to open SWCNTs and DWCNTs during the filling process.

Although various examples of filling have been reported already, filling mechanisms are not well understood yet, especially when considering the molten phase method. Although considering results from previous works suggests that the filling of CNTs could be described by a nanocapillary wetting effect driven by Jurin's law [1,4], factors which may play a role in the filling process are many (e.g., surface tension, viscosity, vapour pressure [1], crystal-nanotube interaction energies [5], etc.) and which ones are the most relevant is not clear yet. In this letter, filling raw DWCNTs (initially closed [6]) with various metal iodides as well as iodine via the molten phase method was performed and the filling rate achieved for each metal iodide was estimated from high-resolution transmission electron microscopy (HRTEM) data. A variety of physical and chemical properties of those iodides were gathered from the literature and their possible influence on the filling rate is discussed.

The filling procedures are described in the Supplementary Information. To estimate the filling rate of each hybrid-DWCNT sample, more than 30 HRTEM images were acquired per sample, from which the filling rate was defined as the ratio of the total length of filled tubes

over the total length of (filled + unfilled) tubes, which is more accurate (even if not perfect) than the simple, visual and global estimation from a series of images which is usually performed. However, due to the inherent limitations of the method used, we estimate that the filling rates are accurate within a  $\pm 5\%$  range (absolute %).

Typical HRTEM images of all the filled DWCNTs are shown in Fig. S1 and it can be seen that the desired filling material was successfully inserted within the nanotubes in each case, confirming the ability of iodine and metal iodides to open CNTs, at least those with a limited number of walls such as DWCNTs.

First of all, the various metal iodides were ranked according to their filling rates, as reported in Table 1 (column 2). It appears that they dispatch into 4 main groups whose filling rates do not overlap taking into account the measurement accuracy:  $\text{NiI}_2$  enables the highest filling rate ( $\sim 50\%$ ), then  $\text{AgI}$ ,  $\text{SnI}_2$ ,  $\text{PbI}_2$  and  $\text{FeI}_2$  belong to a group with filling rates ranging from  $\sim 27$  to  $\sim 38\%$ , then  $\text{CdI}_2$  and  $\text{CoI}_2$  come next with filling rates in the range  $\sim 14$ – $22\%$ , and finally  $\text{LiI}$  and  $\text{KI}$  belong to the last group with filling rates lower than 1%.

Then, physical parameters such as surface tension, viscosity, melting point, boiling point, and vapour pressure of the filling materials were gathered from the literature [7,8] and are also listed in Table 1 (columns 3 to 7). None of them are able to correlate with the filling-rate-based ranking, which is surprising at least for viscosity and surface tension which are presumably important when considering capillarity- and wetting-driven events, as CNT filling mechanisms were supposed to be.

Hence, chemical reactivity was also considered as a possible relevant factor, and redox potential of the couple [metal iodide/metal] was chosen as the parameter to account for it. The redox potential of each corresponding [metal iodide/metal] couple was calculated (i) at the actual experimental filling temperatures for each iodide, and (ii) at the same temperature of  $827^\circ\text{C}$  (see Supplementary Information), which is the highest temperature used among all the filling conditions. Both value series are reported in

**Table 1**

Estimated filling rates and properties of the filling materials. Filling materials are listed according to their filling rate in decreasing order. Column 10 is that considered for the correlation with filling rate (column 2) discussed in the text. However, it is worth noting that considering the redox potential values at actual filling temperatures (column 9) instead of at the maximal temperature of 827 °C (column 10) does not change the four-category ranking revealed and discussed in the text. The same is observed if the Gibbs free energy for the reaction with graphite is considered (column 8).

1	2	3	4	5	6	7	8	9	10			
Filling material	Estimated filling rate (%)	Melting point (°C)	Boiling point (°C)	Surface tension <sup>a</sup> (mJ/m <sup>2</sup> )	Viscosity <sup>a</sup> (mN.s/m <sup>2</sup> )	Vapour pressure <sup>a</sup> (Pa)	Gibbs free energy for the reaction with graphite <sup>b</sup> (kJ/mol) and related ranking	Redox potential <sup>c</sup> at filling temperature (V) and related ranking	Redox potential <sup>c</sup> at 827 °C (V) and related ranking			
NiI <sub>2</sub>	51 ± 5	797	n.a.	54	n.a.	26400	361	<i>1</i>	-0.002	<i>1</i>	-0.002	<i>1</i>
AgI	38 ± 5	558	1506	171	3.58	0.2	545	<i>5</i>	-0.569	<i>4</i>	-0.526	<i>6</i>
SnI <sub>2</sub>	34 ± 5	320	714	43	n.a.	31.8	537	<i>4</i>	-0.613	<i>5</i>	-0.358	<i>4</i>
PbI <sub>2</sub>	32 ± 5	402	953	50	n.a.	22.7	580	<i>6</i>	-0.744	<i>6</i>	-0.489	<i>5</i>
FeI <sub>2</sub>	27 ± 5	587	827	71	n.a.	320	467	<i>3</i>	-0.354	<i>3</i>	-0.298	<i>3</i>
CdI <sub>2</sub>	22 ± 5	387	742	47	17.7	91.5	639	<i>7</i>	-0.855	<i>7</i>	-0.638	<i>7</i>
CoI <sub>2</sub>	14 ± 5	520	570	53	n.a.	8.8	418	<i>2</i>	-0.245	<i>2</i>	-0.139	<i>2</i>
LiI	<1	469	1171	94	2.12	0.1	1434	<i>9</i>	-2.578	<i>8</i>	-2.414	<i>8</i>
KI	<1	681	1330	70	1.6	35.4	1314	<i>8</i>	-2.821	<i>9</i>	-2.749	<i>9</i>
I <sub>2</sub>	27 ± 5	113.7	184.3	37	n.a.	1094					0.000	

na. = not available.

The numbers in italics in columns 8 to 10 represents the ranking numbers deduced from the values for the property within the same column.

<sup>a</sup> All the data are obtained at the melting point of the filling material.

<sup>b</sup> ΔG for reaction 4/xMI<sub>x</sub> + C = 4/xM + Cl<sub>4</sub> (MI<sub>x</sub> is the filling material) at the melting point of the filling material.

<sup>c</sup> For the couple [metal iodide/metal], when relevant (E<sub>I<sub>2</sub>/I<sup>-</sup></sub> is set to 0 V as it is used as a reference couple for the calculations).

**Table 1** (columns 9 and 10 respectively). Since the redox potentials vary with temperature, in order to make relevant the comparison between all the metal iodides, the “redox potential” will always refer to the potential of the couple [metal iodide/metal] at 827 °C in the following, unless clearly stated otherwise. The choice of the highest experimental temperature for the comparison of the redox potentials of the MI<sub>x</sub>/M couples is also dictated by the requirement to have all compounds in the molten state. Considering those redox potential values provides another ranking whose values are listed in decreasing order in the right sub-column of column 10 for easier comparison with the filling rate-based ranking (column 2). From this comparison, it appears that both rankings compare fairly well (yet with a few anomalies):

- The highest filling rate, achieved for NiI<sub>2</sub> (51%), corresponds to the highest redox potential value;
- The large group gathering AgI, SnI<sub>2</sub>, PbI<sub>2</sub>, and FeI<sub>2</sub> (27–38%) corresponds to ranking from #3 to 6 for both the filling rate and the redox potential (while the position of AgI in the list represents a first anomaly);
- The small group including CdI<sub>2</sub> and CoI<sub>2</sub> with low filling rates in the range 14–22% shows the second anomaly: while CdI<sub>2</sub> is ranked #6 and 7 according to the filling rate and redox potential respectively, CoI<sub>2</sub> is ranked #7 according to the filling rate, but is ranked #2 according to the redox potential;
- The lowest filling rates (for KI and LiI: less than 1%) correspond to the lowest redox potentials.

This result shows a good correlation between filling rate and redox potential. This correlation can relate to the need for the tubes to be opened, as the prerequisite for the nanocapillarity-driven filling to occur. Hence, the ability of the filling material in opening the nanotubes is of an utmost importance giving that our starting DWCNTs are initially closed. In a sense, considering that molten halides are supposed to be ionic liquids, redox potential can be considered as an indicator of the reactivity of the halides towards polyaromatic carbon.

The first anomaly regarding the ranking of AgI, which is at the top of its group regarding the filling rate (~38%) but at the bottom of it regarding the redox potential (-0.526 V), could be explained by considering the surface tension values. Indeed, all the metal iodides investigated exhibit surface tension values in the range

43–94 mJ m<sup>-2</sup> except AgI which exhibits a very high value of 171 mJ m<sup>-2</sup>. It is then reasonable to consider that such a difference significantly favors the capillary filling event for AgI with respect to the others: according to Jurin’s law, the height reached by a liquid in a capillary increases with the surface tension of the liquid, for a given capillary diameter [4].

A second anomaly was pointed out above for CoI<sub>2</sub>, since it is ranked #7 according to the filling rate but ranked #2 according to the redox potential. This could be explained by the high propensity of CoI<sub>2</sub> to dimerize even before the melting point is reached [9], assuming that the dimerization is detrimental to the opening and then the filling event (for example by increasing the viscosity as this is the case for polymers when the chain length increases, and also possibly decreasing the reactivity). It is worth noting that a similar behavior was also observed for FeI<sub>2</sub> [10] but its ability to dimerize is lower compared to CoI<sub>2</sub> [11], which is consistent with the observation that the filling rate for this compound is not affected.

Finally, it is also worth noting that NiI<sub>2</sub> exhibits a significantly higher vapor pressure value at the melting temperature compared to all the other metal iodides, and one may wonder which effect this could have with respect to the filling mechanism. This relates to the decomposition reaction of decomposition of NiI<sub>2</sub> into its elements (Ni, I<sub>2</sub>) taking place here before the melting temperature is reached, in accordance with the significantly smaller Gibbs free energy of this reaction (~1.5 kJ/mol) compared to the other metal iodides (ranging from ~27 to 530 kJ/mol, see Table S2). It is therefore likely that the opening of the tubes starts first with gaseous I<sub>2</sub> resulting from the decomposition reaction, and then compete with the opening effect due to molten NiI<sub>2</sub>. Gaseous I<sub>2</sub> may indeed react with the tube to open them and then fill them, as ascertained from the literature [3,12] and the current study. As a result, the material found to fill the DWCNTs was both iodine and NiI<sub>2</sub> (in proportions ~35/65) as ascertained by EELS (see Supplementary Information and related Fig. S2). Therefore, this competition has hindered the actual filling rate that could have been achieved with NiI<sub>2</sub> only, which could have been higher than observed, based on the highest redox potential of this compound within the whole metal iodides series.

In this work, the reactivity of the metal iodides with the DWCNTs resulting in giving access to the tube inner cavity was chosen to be represented by the redox potential values (calculated at the same temperature of 827 °C for all the compounds). One may wonder why not representing it in a more straightforward way

by the Gibbs free energy of the reactions involving graphitic carbon and the different metal halides, resulting in the formation of carbon tetraiodide  $\text{CI}_4$  at the corresponding melting temperature. The problem is that, once calculated (see Table 1, column 8) the related  $\Delta G$  values for this reaction are all positive, suggesting that the related reactions are all thermodynamically infeasible. However, it is clear from our experiments and previous ones from the literature [3,12] that iodine, either gaseous or molten, is able to open and then fill DWCNTs (and SWCNTs). The reason for this apparent contradiction probably comes from the fact that in available thermodynamics databases, data related to  $sp^2$ -hybridized carbon is represented by genuine graphite, which is far from being valid for CNTs, and specifically for DWCNTs and SWCNTs. First,  $sp^2$  carbon networks in DWCNTs and SWCNTs are bent following a nanometer-range radius of curvature, and second, according to Euler's rule, carbon nanotubes include 6 pentagons at each tip in order to close the nanostructure. For both configurations (*i.e.*, "bent graphene", and pentagons), C–C bonds are heavily strained (specifically in pentagons), which is known to enhance their reactivity [13], and then is likely to turn the free Gibbs energy of the reaction with metal iodides down to negative values. Hence, future work will have to use theoretical values for bent graphene with fullerenoid (*i.e.*, containing pentagonal rings) tube caps instead of graphitic carbon, also taking into consideration the facts that different bending angles may be used (because there is a diameter distribution in our host DWCNT material) along with various pentagon orientations and locations [14].

In summary, direct filling of initially closed DWCNTs with various iodides was performed and the relationships between presumably relevant physical and chemical properties of the iodides and the filling rate were investigated. It is found that the filling rate is mostly driven by the redox potential of the [metal iodide/metal] couple of the filling material at the molten state, which relates to the reactivity of metal iodides towards carbon, thanks to the enhanced reactivity of carbon when involved in DWCNTs (and SWCNTs). Therefore, the ranking based on the filling rate and that based on the redox potential are fairly well related. Few anomalies in the correlation exist, though, which can be explained by considering other parameters such as surface tension, vapor pressure, or ability to dimerize or decompose. Further work on similar investigations involving other halides, and other compounds should now be carried out, but the fact that not all the data (*e.g.*, viscosity at melting temperature) are available in the literature and that thermodynamics databases only consider carbon in the regular graphitic form slows down significantly the progress in the field.

## Acknowledgements

The author thanks the financial support of China Scholarship Council (Scholarship number: #201306140037). We thank P. Chamelot and L. Cassayre for help with providing access to thermodynamics database. We also thank L. Datas (R. Castaing characterization platform, UMS 3623) for his help with HRTEM observations and EELS analysis.

## Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://>

[dx.doi.org/10.1016/j.carbon.2016.09.001](http://dx.doi.org/10.1016/j.carbon.2016.09.001).

## References

- [1] M. Monthieux, E. Flahaut, J.-P. Cleuziou, Hybrid carbon nanotubes: strategy, progress, and perspectives, *J. Mater. Res.* 21 (2006) 2774–2793.
- [2] G. Brown, S. Bailey, M. Novotny, R. Carter, E. Flahaut, K. Coleman, et al., High yield incorporation and washing properties of halides incorporated into single walled carbon nanotubes, *Appl. Phys. A* 76 (2003) 457–462.
- [3] X. Fan, E.C. Dickey, P. Eklund, K. Williams, L. Grigorian, R. Buczko, et al., Atomic arrangement of iodine atoms inside single-walled carbon nanotubes, *Phys. Rev. Lett.* 84 (2000) 4621–4623.
- [4] P.-G. de Gennes, F. Brochart-Wyart, D. Quéré, Droplets, Bubbles, Pearls, and Waves, Belin, Paris (, 2002 (In French).
- [5] E.L. Sceats, J.C. Green, S. Reich, Theoretical study of the molecular and electronic structure of one-dimensional crystals of potassium iodide and composites formed upon intercalation in single-walled carbon nanotubes, *Phys. Rev. B* 73 (2006) 125441.
- [6] E. Flahaut, R. Bacsa, A. Peigney, C. Laurent, Gram-scale CCVD synthesis of double-walled carbon nanotubes, *Chem. Comm.* (2003) 1442–1443.
- [7] G.J. Janz, Thermodynamic and Transport Properties for Molten Salts: Correlation Equations for Critically Evaluated Density, Surface Tension, Electrical Conductance, and Viscosity Data, The American Chemical Society and the American Institute of Physics for the National Bureau of Standards, New York (, 1988.
- [8] F. Agra, Surface tension of molten metal halide salts, *J. Mol. Liq.* 200 (2014) 120–121.
- [9] S.D. Hill, C. Cleland, A. Adams, A. Landsberg, F.E. Block, Vapor pressures and heats of sublimation of cobalt dihalides, *J. Chem. Eng. Data* 14 (1969) 84–89.
- [10] W. Zaugg, N. Gregory, Thermodynamic properties of  $\text{FeI}_2$  (g) and  $\text{Fe}_2\text{I}_4$  (g), *J. Phys. Chem.* 70 (1966) 490–494.
- [11] N. Schiefenhövel, M. Binnewies, F. Janetzko, K. Jug, Zur thermodynamik des dimerisierung von gas förmigem  $\text{CrI}_2$ ,  $\text{MnI}_2$ ,  $\text{FeI}_2$  und  $\text{CoI}_2$ : experimentelle und quantenchemische untersuchungen, *Z. Anorg. Allg. Chem.* 627 (2001) 1513–1517 (In German).
- [12] L. Guan, K. Suenaga, Z. Shi, Z. Gu, S. Iijima, Polymorphic structures of iodine and their phase transition in confined nanospace, *Nanoletters* 7 (2007) 1532–1535.
- [13] Y. Chen, R.C. Haddon, S. Fang, A.M. Rao, P.C. Eklund, W.H. Lee, et al., Chemical attachment of organic functional groups to single-walled carbon nanotube material, *J. Mater. Res.* 13 (1998), 2423–2331.
- [14] I. Suarez-Martinez, J. Mittal, H. Allouche, M. Pacheco, M. Monthieux, M. Razafinimanana, et al., Fullerene attachment to sharp-angle nanocones mediated by covalent oxygen bridging, *Carbon* 54 (2013) 149–154.

Chunyang Nie

*CIRIMAT, UMR-5085 CNRS, Université de Toulouse, France*

*CEMES, UPR-8011 CNRS, Université de Toulouse, France*

Anne-Marie Galibert, Brigitte Soula, Emmanuel Flahaut  
*CIRIMAT, UMR-5085 CNRS, Université de Toulouse, France*

*E-mail address: flahaut@chimie.ups-tlse.fr* (E. Flahaut).

Jeremy Sloan

*Department of Physics & Warwick Centre for Analytical Science,  
University of Warwick, Coventry, UK*

Marc Monthieux\*

*CEMES, UPR-8011 CNRS, Université de Toulouse, France*

\* Corresponding authors.

*E-mail address: marc.monthieux@cemes.fr* (M. Monthieux).