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Comment on “*Carbon nanotube/graphene composite for enhanced capacitive deionization performance*” by Y. Wimalasiri and L. Zou

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Abstract

In a recent study, Wimalasiri and Zou [1] have reported the use and performance of composite electrodes of carbon nanotubes (CNT) and graphene for application as porous electrodes in capacitive deionization (CDI). While CDI is emerging as an attractive technology for water desalination, and novel electrode materials and composites are important contributions to the advancement of the field, there are several issues in this study that we must comment on.

We first address the capacitive deionization performance reported by Wimalasiri and Zou [1], namely an adsorption of NaCl in the composite electrodes of 26.42 mg/g at a cell voltage of V_{cell} = 2.0 V. This value is approximately one order of magnitude higher than what has been reported for this kind of composite material in 2012 by Zhang et al. [2], namely 1.4 mg/g at V_{cell} = 2.0 V, and very recently by Li et al. [3], namely 0.9 mg/g at V_{cell}=1.6 V. The difference in performance is in contrast to the very similar synthesis route of all three studies (i.e., reduction of graphene oxide / CNT composite) and the comparable pore characteristics of the composite electrode (Zhang et al.: 480 m^2/g; Li. et al.: up to 450 m^2/g; Wimalasiri and Zou: 391 m^2/g).

As these two examples show, in previous literature, values for salt adsorption in electrodes composed of graphene, CNTs, or composites thereof, are all very close and in the low range 1-3 mg/g, defined per g of both electrodes combined, see Table 1. Such moderate performance is in line with expectations, because the specific surface area of these materials is moderate (i.e., a few hundred m^2/g). In contrast, the much higher salt adsorption capacity in CDI known for microporous carbons occurs in conjunction with high specific surface areas in excess of 1000 m^2/g [4, 5]. Thus, it remains unclear how the material reported by Wimalasiri and Zou with a specific surface area below 400 m^2/g and pores in the range of 3-4 nm for graphene and 7-8 nm for CNT / graphene composites would provide such a high salt adsorption capacity and high capacitance (220 F/g = 0.56 F/m^2). We like to note that the stated salt adsorption capacity of 26 mg/g is per gram of CNT/graphene, and not per gram of total electrode, which would reduce the number to 19 mg/g because 28 mass% of the total electrode is composed of binder and graphite.

Furthermore, the authors state that > 88% of the CNT / graphene electrode could be regenerated by a simple short circuit without the reversal of charge. However, outside of the first one or two desalination cycles, and except for a sudden degradation of the electrode, regeneration should always be 100%. A lower regeneration would cause an ever-increasing salt accumulation in the electrode material from cycle to cycle, a non-physical result. In our opinion, the reported value of > 88% is a sign that either the mass balance calculation is incorrect or of device failure (e.g., of the conductivity probe). Further, we disagree with the statement by the authors that complete regeneration of the composite electrode was a measure of high performance (see last line of abstract). Instead, full regeneration is a direct result of mass conservation, and so can also be obtained for a cell with very low salt adsorption capacity (i.e. poor performance). Instead, a more reliable measure for CDI performance is the change of the salt adsorption capacity with ongoing cycling.

Table 1: Selected CDI performance of carbon electrodes composed of CNT, graphene, or carbide-derived carbon (i.e., microporous carbon).

Material used	V_{cell} **(V)**	**Salt adsorption (mg/g)**	**Reference**
CNT (single-walled)	2.0	0.75	[6]
Graphene	2.0	1.3	[7]
CNT / graphene	2.0	1.4	[2]

CNT (double-walled)	2.0	0.55	[6]
CNT	1.2	1.7	[8]
Graphene	2.0	1.9	[9]
CNT/carbon nanofibers	1.2	3.3	[10]
Carbide-derived carbon	1.2	12.4	[4]

Another statement made in Section 3 is that addition of CNTs reduces the electrical resistivity of the graphene electrode, and this is expected to also lead to an improved electrosorption capacity. Analogously, in the Abstract the authors stated how the rapid ion conduction for the composite electrodes has an associated higher EDL capacitance and capacitive deionization performance. However, it must be noted that electrical resistivity and ion conduction (ion conductivity) on the one hand, and EDL capacitance and salt electrosorption capacity on the other hand are very different concepts, with the first one dealing with kinetics, the latter with (equilibrium) capacity. To the best of our knowledge, there is no study showing an unambiguous positive correlation between these two concepts for CDI. Only for short experiments, do the electrical and ionic resistance play a role in the measured, apparent adsorption capacity of a CDI cycle. But, the data provided by Wimalasiri and Zou in their *Fig. 7* suggest that equilibrium in fact was approached. In addition, given that the electrical resistivity of the composite electrode was lower than of the electrode composed only of graphene, there is no evidence that the higher kinetics of salt adsorption as reported in *Fig. 7* is (also) due to higher ion conductivity.

Wimalasiri and Zou discuss the improved performance of the composite electrode versus the pure-graphene electrode at various points suggesting that with the addition of CNTs, the desalination capacity has improved by roughly 20% (compared to 22 mg/g for the pure graphene electrode). This statement, however, is not supported by a sufficient number of independent experimental data points. We note that the entire comparison is based on one reported data point for desalination performance for each material (each curve in *Fig. 7*) and there is no evidence of duplicate or triplicate experiments. For a reliable comparison between two materials, performing duplicate or even triplicate experiments (starting each time from a new batch of synthesized material) is required. Otherwise, any experimental error in synthesis or cell construction (which in our experience is very well possible and may yield an error in excess of 20%) may lead to erroneous conclusions.

Our final comment concerns the statement that the regeneration of CNT / graphene electrodes becomes faster with cycling lifetime, whereas the graphene electrode was regenerated more slowly over multiple cycles. This statement is not supported by the data shown in *Fig. 7*. Instead for CNT/graphene, it is observed that the first and fourth cycle have a somewhat slower regeneration than the second and third cycle, but basically for both electrode types we see no change at all. If by “better cycle life” the authors mean “long term stability”, we must disagree with this interpretation. Instead, the data only show stable behavior for four cycles for the composite electrode, and for only two cycles for the pure-graphene electrode, for a total duration of the experiment of just 4 h.

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