EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

	Experiment title: **temperature dependent swelling transitions in Hummers graphite oxide immersed in excess of liquid 1-alcohol**	**Experiment number**: HC-5403
Beamline: ID22	**Date of experiment**: from: 15 September 2023 to: 18 September 2023	**Date of report**: 13 Dec.2023
Shifts: 12	**Local contact(s)**: Catherine Dejoie	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Alexandr Talyzin,* Department of Physics , Umeå University, Sweden

Report:

According to proposal the experiment plan included XRD study of Hummers Graphite Oxide (HGO) structure for samples immersed in excess of liquid chain alcohols. First priority was given to experiments with HGO in alcohols named in following according to the number of carbon atoms in the chain starting from methanol (C3) and all progressively longer alcohols up to C13. We also recorded data for HGO in methanol and ethanol (previously studied and publsihed) in order to have the data of the same quality for the whole set. Th etemperature interval of interest for this study is starting from melting point of alcohol and up to ~100^0C. Higher temperatures might result in thermal degradation of GO. Therefore, we recorded heating-cooling cycles starting from temperatures slightly below melting point of alcohols up to 370K (somewhat lower for methanol and ethanol due to low boiling points of these solvent).

It was expected that swelling transition will be observed for alcohols with C>9 and gradual changes of interlayer distance for smaller alcohols. Adding these data to already collected preliminary results for longer alcohols (C14 to C20) was needed in order to complete analysis of HGO swelling in the whole rather long set of 1-alcohols providing information about fundamental trends. Experiments were performed as planned and the data were recorded for HGO in the whole set from C1 to C13. The data are processed by the time of writing this report and d(001) is found for all patterns using batch fitting. Individual figures showing selected XRD patterns as a funtion of temperature for each HGO-alcohol system will also be prepared for publication.

The d(001) corresponds to the distance between graphene oxide layers in the graphite oxide structure and it changes dramatically when material is immersed in liquid alcohols due to effect of swelling. The swelling at ambient temperature is found to be progressively stronger for longer alcohols. The swelling of HGO is also found to show dramatic changes upon temperature increase/decrease. The summary of all data available by now is shown in the **Figure 1**. The data provide first evidence for rather different types of HGO swelling in long and short alcohols with the change around C9. HGO immersed in liquid alcohols with chain length C10 and longer exhibit sharp transition with step-like decrease of d(001) upon heating. The swelling transition of this type was found previously in BGO-alcohol systems[1, 2] and corresponds incongruent melting of low temperature phase with two layers of alcohol molecules in perpendicular to GO planes orientation with formation of high temperature phase with several layers of alcohol moelcules parallel to GO planes. We suggest that the phase transitions on HGO-alcohols C10-C22 are of similar nature.

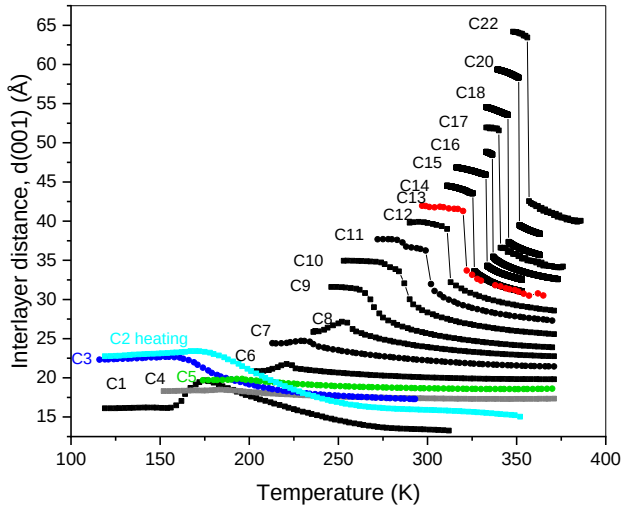

Figure 1. Temperature dependence of inter-layer distance for HGO in a set of 1-alcohols with progressively longer chain length (C1 to C13). The data recorded previously are added to show the general trends (>C13).

Temperature dependence of d(001) for HGO immersed in short alcohols (C1 to C8) shows is distinctly different. Continous change of d(001) as a function of temperature observed for HGO in these alcohols was asisgned previously to effects of interstratification. Until our new experiments it was reported only for HGO in methanol (C1) and ethanol (2).[3] This type of temperature dependence of swelling is also ver different compared to swelling of BGO in the same alcohols.[4, 5] BGO exhibited swelling transitions related to change in the number of intercalated alcohol layers and absence of strong continous changes revealed in our new experiments. Rather non-trivial differences in the temperature dependence of swelling are found in our experiments with HGO in small alcohols. It is not clear at the moment why e.g. swelling in C2 and C3 so strongly depends on temperature, while C4 shows almost flat curve (Fig.1). Our initial assumption is that intercalation of alcohols C1 to C8 occurs with formation of layers parallel to HGO planes but the nature of difference between temperature dependence in each individual alcohol is not yet clear.

In summary, as anticipated from our earlier studies, two types of temperature dependent swelling are found for HGO in alcohols larger and smaller than C9. The XRD data will be combined with characterization of swelling transitions and sorption of alcohols by HGO just above the melting point of alcohol by DSC method.

The data shown in Fig.1 are completely novel for alcohols C3 to C22 and will be used for high quality publication after additional complimentary characterizations by other methods.

1. Nordenström, A.; Iakunkov, A.; Boulanger, N.; Li, G.; Hennig, C.; Baburin, I.; Jorgensen, M.; Kantor, I.; Talyzin, A. V., Temperature dependent intercalation of molten 1-hexadecanol into Brodie graphite oxide. *Carbon* **2023,** *203*, 770-784.
2. Iakunkov, A.; Nordenström, A.; Boulanger, N.; Li, G.; Hennig, C.; Jorgensen, M. R. V.; Kantor, I.; Talyzin, A. V., Effect of Chain Length on Swelling Transitions of Brodie Graphite Oxide in Liquid 1-Alcohols. *Adv Mater Interfaces* **2023**.
3. You, S. J.; Sundqvist, B.; Talyzin, A. V., Enormous Lattice Expansion of Hummers Graphite Oxide in Alcohols at Low Temperatures. *Acs Nano* **2013,** *7* (2), 1395-1399.
4. You, S. J.; Luzan, S.; Yu, J. C.; Sundqvist, B.; Talyzin, A. V., Phase Transitions in Graphite Oxide Solvates at Temperatures Near Ambient. *J Phys Chem Lett* **2012,** *3* (7), 812-817.
5. Klechikov, A.; Sun, J. H.; Baburin, I. A.; Seifert, G.; Rebrikova, A. T.; Avramenko, N. V.; Korobov, M. V.; Talyzin, A. V., Multilayered intercalation of 1-octanol into Brodie graphite oxide. *Nanoscale* **2017,** *9* (20), 6929-6936.