Insights into permeation properties of GO and rGO films.

Alba María Fernández-Sotillo, Antonio M. Chaparro, Paloma Ferreira-Aparicio.
Department of Energy, CIEMAT.
Avenida Complutense 40. E-28040 Madrid, Spain.

Introduction

Graphene materials are recently finding very interesting applications in innumerable technological fields as result of their particular properties. Membrane technology is one of these fields of interest, in particular for graphene oxide (GO) and reduced graphene oxide (rGO). Reduced GO membranes have been reported to allow unimpeded permeability to water, whereas they can be leak-tight to gases such as helium.
In this study, the permeation properties of GO and rGO membranes to fluids have been evaluated and are presented Together with their morphological and physicochemical characterization.

Scientific Approach

GO membranes have been prepared from commercial GO aqueous dispersion. PTFE plates have been used to deposit amounts of GO suspension in a given concentration depending on the required GO film thickness. The suspension was dried under natural convection of air at room temperature. The resulting films were submitted to different treatments to analyze the changes in the mille-feuille-like laminar structure. The observed changes are correlated with the permeation properties for fluids.

Tests performed:

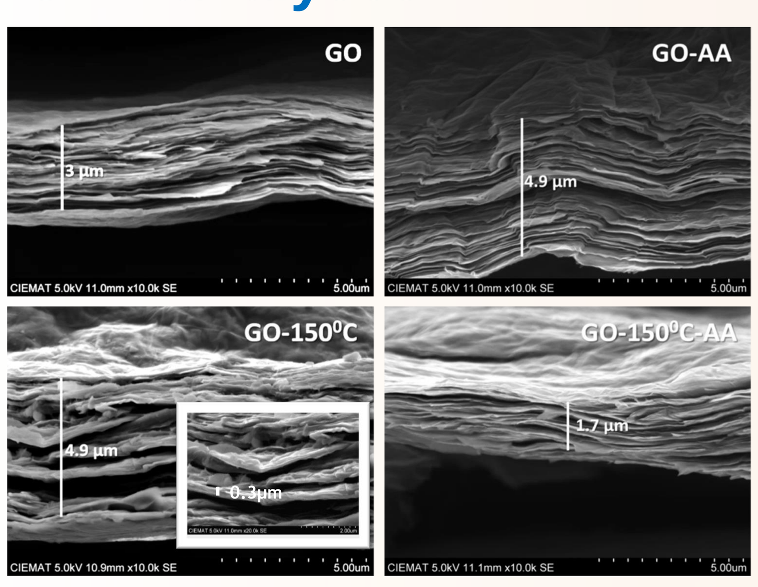
- **GO films pretreatments:**
  - **None, as prepared (GO)**
  - **Reduction in ascorbic acid solution (GO-AA)**
  - **Heating at 150ºC (GO-150ºC)**
  - **Heating at 150ºC and subsequent reduction with AA solution (GO-150ºC-AA)**
- **Permeability measurements**

Characterization analyses:

- **SEM (cross-section observation)**
- **XRD**
- **XPS**
- **ATR**

Characterization of the films

SEM analyses



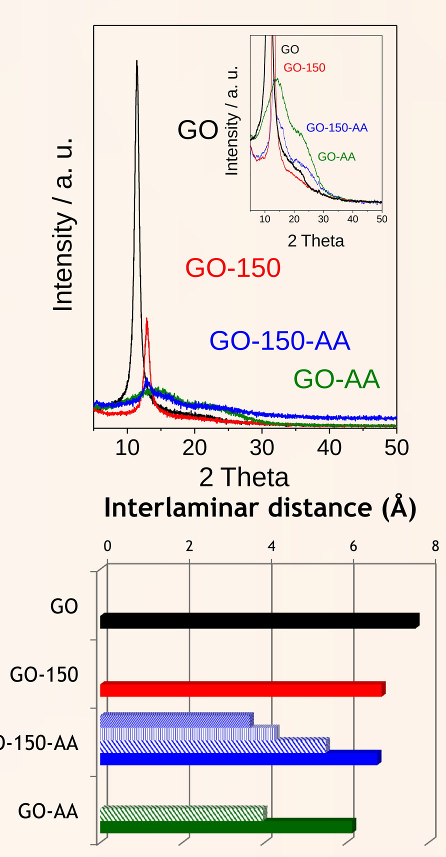
Images of the same film cross-section submitted to different treatments: as prepared (GO), reduced (GO-AA), heated (GO-150ºC) and, heated and reduced (GO-150ºC-AA). The applied treatment leads to the expansion or constriction of the observed mille-feuille-like structure. Grouped GO layers of about 0.3 µm thickness are stacked in sheets in the range between 1 and 5 µm.

The heating treatment at 150ºC reduces slightly the interlaminar distances between GO platelets as revealed by XRD. SEM imaging indicates that the platelets become stacked in multilayer laminates with thicknesses below 0.1 µm yielding a total thickness of *ca.* 5 µm.

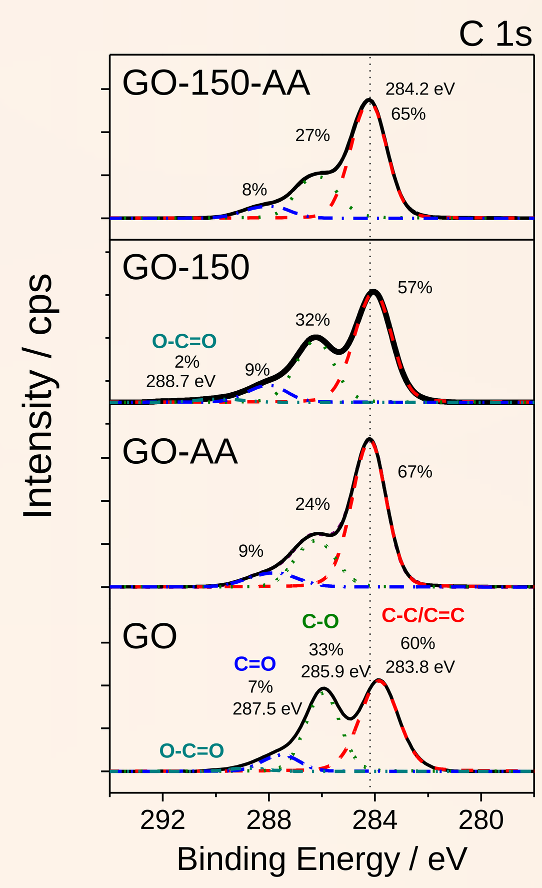
Heating seems to modify the distribution of carbon-oxygen functional groups although does not change the oxygen content.

The treatment with ascorbic acid solution reduces partially the oxygen content in the GO films and removes substantially oxygenated surface groups, although some of them still remain on their surface.

XRD



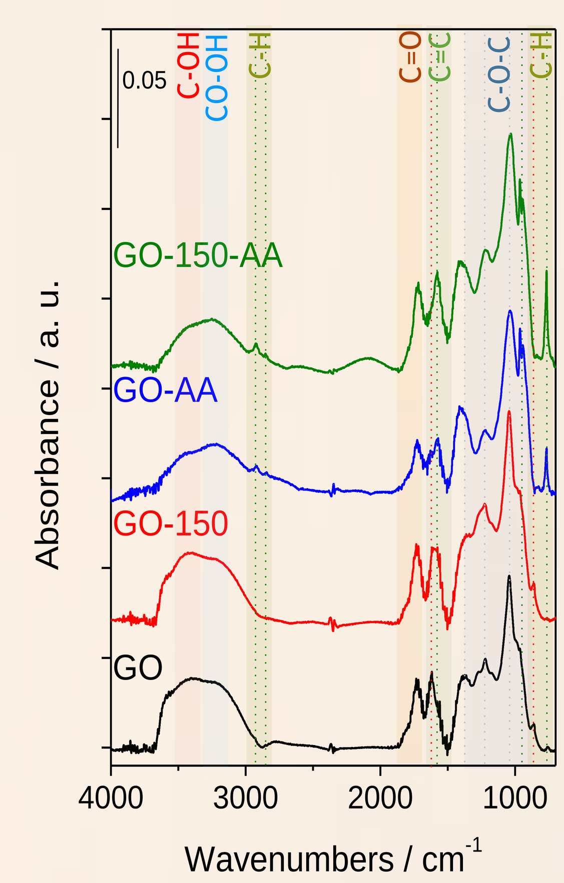
XPS analyses



Surface composition by XPS analysis

Sample	C (%)	O (%)	S (%)
GO	76.9	22.7	0.4
GO-150	76.5	22.9	0.6
GO-AA	81.2	18.7	0.1
GO-150-AA	81.1	18.7	0.2

ATR-FTIR analyses



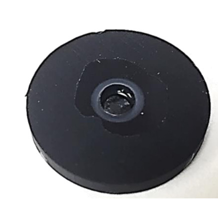
Permeability measurements

Design and fabrication of a permeation cell by additive manufacturing, using stereolythography.

Mounting plate

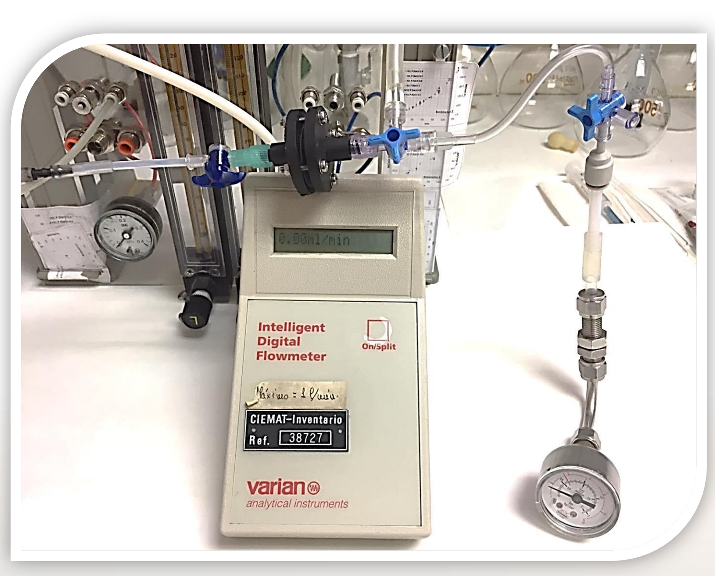
GO film sealing

Mounted GO sample

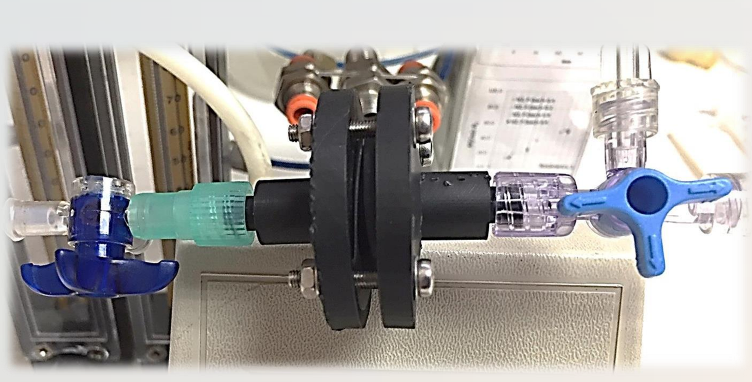


Sample holder:
ID: 7mm
OD: 24 mm
Permeation area: 38.5 mm²

Gas permeation system



Permeation cell



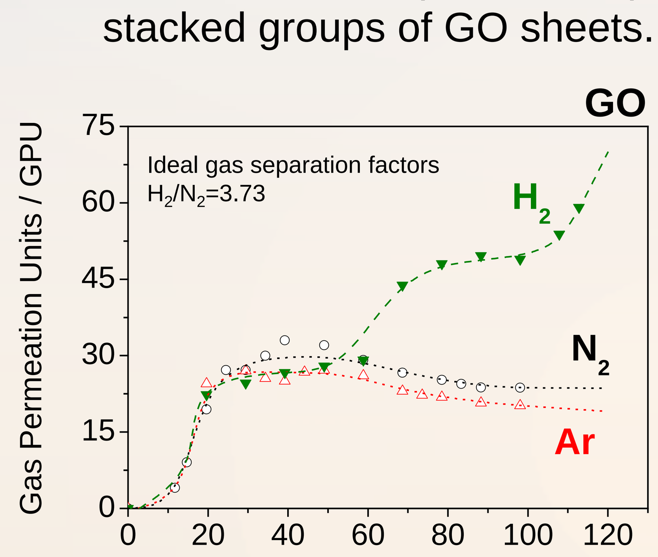
Gas permeation tests

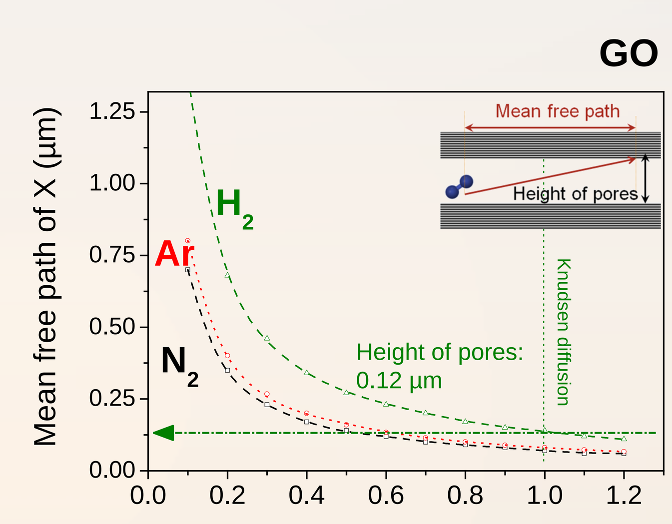
GO-AA / GO-150 / GO-150-AA membranes

- Gas-tight membranes checked for N_2 and H_2 up to 1.1 bar over pressure.
- They are resistant up to 1.5 bar transmembrane pressure.

GO membrane

- Initially the membrane was gas-tight with no leaks at pressures below 0.15 bar. After some time the membrane allowed some gas permeation.
- Gas permeance was measured for N_2, Ar and H_2 up to 1 bar transmembrane pressure.
- Permeance approximated Knudsen diffusion at transmembrane pressures above 1 bar (100 kPa): that means that under those conditions the scale length of the membrane pores are comparable to the mean free path of the particles involved passing between stacked groups of GO sheets.





Water permeation system

Water permeation tests

- **Dry membrane:** Initially no water permeation is allowed.
- **After water contact for 2 h:** Water permeation is completely allowed.

Measurements performed applying the force of a column of water over the film.

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