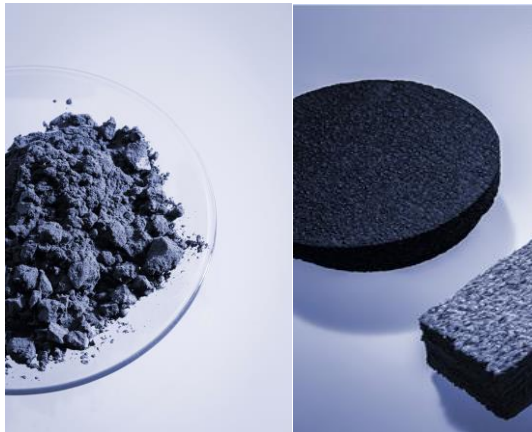


## Surface zeta potential analysis of novel graphene oxide coatings for membranes

Relevant for: graphene, graphene oxide, membranes, surface charge, zeta potential

2D materials such as graphene and graphene oxide introduce new pathways for the development of novel materials with superior properties. Nanocomposite coatings containing graphene oxide are investigated for their capability to enhance the performance of membranes for water treatment applications. We use the analysis of the zeta potential to confirm the presence of graphene oxide at the surface of such nanocomposite membrane coatings, which is a requirement for their activity and interaction with the aqueous environment.



### Introduction

The discovery of graphene has opened completely new technological pathways in material science. Nowadays graphene and its derivatives can be found in a large number of applications due to their outstanding properties. Such applications can be found in the fields of electronics and batteries but also in biomedical applications including drug delivery, biosensing, bioimaging, and scaffolds for tissue engineering.

The hydrophilic nature of graphene oxide makes this graphene derivative also attractive for the advancement of membrane technology. Graphene oxide is expected to increase the water permeability, to suppress membrane fouling, and to introduce a reinforcement of polymer membranes.

We report on the modification of a polymer membrane by a graphene oxide-polyelectrolyte composite coating and its effect on the charging behaviour at the membrane-water interface. A second example considers the formation of a ceramic membrane composed of graphene oxide and aluminium oxide.

The characterization of the surface and interfacial charge of polymer and ceramic membranes employs the measurement of the streaming potential for the calculation of the surface zeta potential.

### Graphene oxide composite membranes

Graphene with its two-dimensional planar structure increases the mechanical strength, the thermal stability and the electrical properties of composites, and has thus received attention as a suitable candidate for the development of membranes for water treatment processes. In contrast to graphene, graphene oxide (GO) exhibits an increased hydrophilicity due to the oxygen-containing functional groups (C=O, C-OH). The latter lead to a better dispersion of GO in water and other polar solvents thereby maintaining the superior properties of graphene. The amphiphilic character of GO makes it compatible with polymers, which are used as the base material in the low-cost membrane production process, and enhances the water permeability and the antifouling properties of membranes. Additionally, graphene and GO are low-cost alternatives to carbon nanotubes (CNT) or carbon nanofibers (CNF).

These properties make GO a potential modifier for polymer but also ceramic membranes for wastewater treatment processes.

### Membranes and the zeta potential

The zeta potential is a solid-water interfacial parameter and representative for the material surface charge. The zeta potential helps to predict electrostatic interactions between material surfaces and solutes in a surrounding aqueous solution. Furthermore, the analysis of the zeta potential is a sensitive method to detect changes in the surface chemistry. In the field of membrane applications, the

zeta potential contributes to the rejection of solutes and to membrane fouling. With the help of zeta potential analysis, it is possible to determine the coverage of the membrane surface by a thin-film coating and the stability of such coating.

## Experimental

Two types of nanocomposite coatings containing graphene oxide were prepared as potential candidates for novel membrane materials. A multilayer coating with alternating layers of GO and the cationic polyelectrolyte polyethylenimine (PEI) was deposited on a flat sheet polymer ultrafiltration membrane. A second nanocomposite coating was of ceramic nature and composed of GO and nanocrystalline aluminium oxide ( $\text{Al}_2\text{O}_3$ ).

The instrument SurPASS 3 was used for the zeta potential analyses of flat sheet membranes with different GO nanocomposite coatings. Small sample pieces of 20 mm x 10 mm were adhered to the sample holders of the Adjustable Gap Cell with the active coating facing upwards (Figure 1).

Streaming potential measurements were performed with an aqueous 0.001 mol/l KCl solution used as the background electrolyte. The pH dependence of the zeta potential was recorded automatically with the integrated dosing unit to determine the isoelectric point (IEP, pH value where the zeta potential is 0 mV and a charge reversal takes place) of each GO coating.



Figure 1: Left: SurPASS 3 equipped with dosing unit. Right: Adjustable Gap Cell with sample holders with a cross-section of 20 x 10 mm<sup>2</sup>.

## Results

### GO coating on a polymer membrane

The combination of GO nanoparticles with the cationic polyelectrolyte poly(ethylene imine), PEI, was used to improve the rejection of a polyacrylonitrile membrane (PAN) for ultrafiltration (UF) thereby maintaining the high water permeability [1]. Figure 2 shows the pH dependence of the zeta potential for such a PAN UF membrane with a GO | PEI coating deposited by a layer-by-layer method. Above the IEP at pH 3.3, the

coating is negatively charged with the zeta potential approaching  $\zeta = -40$  mV at neutral and alkaline pH.

In order to interpret the observed zeta potential as a representative for the surface charge of the GO | PEI coating and to understand the composition of this coating, Figure 2 also displays the zeta potential for a pristine PAN membrane, for the PAN membrane coated solely with PEI, and for a membrane coated with a stand-alone film of GO.

We find significant differences in the zeta potential for each of these membrane samples. Although the zeta potential and therefore the electrokinetic charge density  $\sigma_{ek}$  of the pristine and GO | PEI-coated PAN membranes are similar at pH 8-9 ( $\zeta \sim -40$  mV,  $\sigma_{ek} \sim -0.34 \mu\text{C}/\text{cm}^2$ ), the pH dependences and the isoelectric points give evidence for the modification of PAN by the GO | PEI coating.

The sole coating of the PAN membrane by the cationic polyelectrolyte PEI shifts the IEP from pH 4.6 for the pristine PAN membrane to pH 8.9. The secondary amine groups of PEI get protonated at low and medium pH. Due to their strongly basic character, rather highly alkaline conditions are required to suppress this protonation. At pH 8.9 of the bulk aqueous solution we find an electroneutral condition at the membrane-water interface and thus the IEP for the PEI-coated PAN membrane. Since the IEP for the GO | PEI-coated membrane is shifted to even lower pH compared to the IEP of PAN, we conclude that PEI obviously does not contribute to the charge at the outermost surface of the GO | PEI coating.

A comparison of the zeta potential for the GO | PEI-coated PAN membrane with the zeta potential for a stand-alone membrane of graphene oxide reveals the apparent nature of the GO | PEI coating, which is dominated by the presence of GO. Obviously the layer-by-layer coating achieves a well separated stack of polymer (PEI) and GO layers with GO determining the terminal layer.

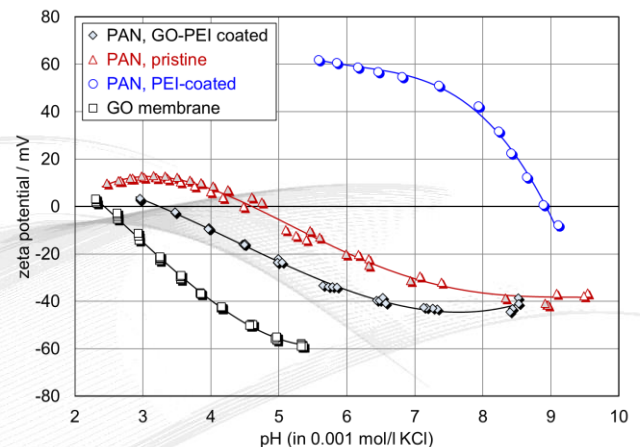


Figure 2: pH dependence of the zeta potential for a pristine polyacrylonitrile (PAN) membrane for UF, for the PAN membrane coated with a multilayer of GO and PEI, for a PEI-coated PAN membrane, and for a GO membrane.

## GO | Al<sub>2</sub>O<sub>3</sub> composite membrane

In another example we use the same zeta potential results for a membrane coated with a stand-alone porous film of GO shown in Figure 2 to explain the composition of a composite layer of GO and Al<sub>2</sub>O<sub>3</sub>. Figure 3 shows the pH dependence of the zeta potential for such a GO|Al<sub>2</sub>O<sub>3</sub> coating and compares this result with the zeta potential of the GO coated membrane and with the zeta potential obtained for a single-channel tubular alumina ceramic membrane for microfiltration (MF). While all measurements of the streaming potential for flat membrane surfaces employ the Adjustable Gap Cell, the zeta potential analysis of the microporous ceramic membrane utilizes the measuring cell for tubular membranes [2]. The IEP 5.2 of the GO | Al<sub>2</sub>O<sub>3</sub> composite layer is found in between the IEP 2.4 for the GO stand-alone film and the IEP 6.5 for the alumina MF membrane. To conclude on the composition of the GO | Al<sub>2</sub>O<sub>3</sub> layer, we first elucidate the zeta potential of the Al<sub>2</sub>O<sub>3</sub> ceramic membrane. For this purpose, we add another dependence of the zeta potential on the pH of the aqueous KCl solution, which was obtained for a sample plug of corundum powder. The difference in the IEPs of  $\Delta\text{pH} = 1.5$  for corundum powder and the alumina membrane may be explained by an ageing effect for the membrane surface. Note that the surface of Al<sub>2</sub>O<sub>3</sub> exhibits a rather complex behaviour and the IEP may range from pH 4 for single-crystalline sapphire [3] to pH > 9 for Al<sub>2</sub>O<sub>3</sub> nanoparticles in dispersion [4].

For the interpretation of the composition of the outermost surface of the GO | Al<sub>2</sub>O<sub>3</sub> layer, we refer to the IEP 8 of corundum powder and to the IEP 2.4 of the purely GO membrane. Based on the comparison of these materials and their IEPs, we conclude on a homogeneous composition of the layer with a contribution of 50% by GO and 50% by Al<sub>2</sub>O<sub>3</sub>.

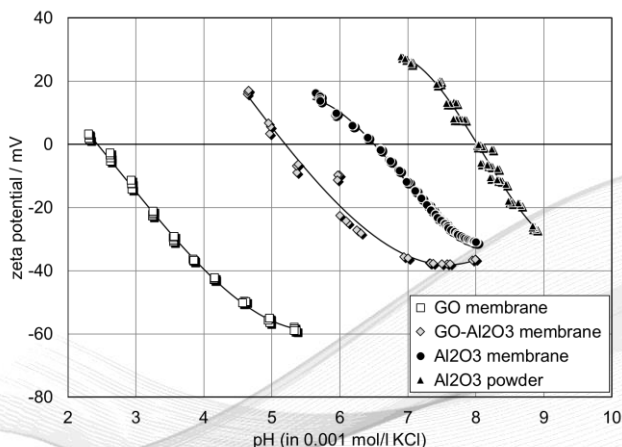


Figure 3: pH dependence of the zeta potential for a GO|Al<sub>2</sub>O<sub>3</sub> nanocomposite coating, a stand-alone film of GO on a membrane, and two samples of Al<sub>2</sub>O<sub>3</sub> (a single-channel tubular ceramic MF membrane and corundum powder).

## Summary

New generation 2D materials such as graphene oxide offer a high potential for the development of novel materials with advanced properties. The tunability of GO makes it a promising candidate for the modification of membranes for water treatment to improve the water transport and to suppress membrane fouling. The transfer of knowledge about the correlation of the surface zeta potential with salt rejection and the fouling propensity of (primarily) polymer membranes, which was developed in the past decades, to the characterization of novel coatings containing GO is straightforward. This report illustrates results for graphene oxide and GO-containing surface coatings for both polymeric and ceramic films. The IEPs summarized in Table 1 demonstrate the variability of surfaces prepared by using GO as a composite material. A comparison of the IEP of the composite material with the IEPs of the individual components enables an estimation of the surface composition. The derived contribution of GO of the composite layers to the zeta potential is also shown in Table 1.

Table 1: Isoelectric points of materials discussed in this report and surface contribution of GO to composite layers

Sample	IEP	GO contribution
GO membrane	2.4	100 %
PAN membrane	4.6	n/a
GO   PEI LbL-coated PAN	3.3	85 %
PEI-coated PAN	8.9	n/a
GO-Al <sub>2</sub> O <sub>3</sub> composite	5.2	50 %
Al <sub>2</sub> O <sub>3</sub> MF membrane	6.5	n/a
Corundum powder	8	n/a

## References

- Andreeva, D.V., Trushin, M., Nikitna, A. et al. Two-dimensional adaptive membranes with programmable water and ionic channels. *Nat. Nanotechnol.* 16 (2) (2021) 174-180, <https://doi.org/10.1038/s41565-020-00795-y>
- Application report XPCIA005EN. From pottery to membranes: Characterization of ceramic powders and surfaces. Anton Paar GmbH, 2020
- Lützenkirchen, J., Zimmermann, R., Preocanin, T. et al. An attempt to explain bimodal behaviour of the sapphire c-plane electrolyte interface. *Adv. Colloid Interface Sci.* 157 (1-2) (2010) 61-74, <https://doi.org/10.1016/j.cis.2010.03.003>
- Kosmulski, M. The pH-dependent surface charging and the points of zero charge. *J. Colloid Interface Sci.* 253 (1) (2002) 77-87, <https://doi.org/10.1006/jcis.2002.8490>

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