

Li⁺-Doping of Polyelectrolyte Multilayers for Enhanced Ionic Conductivity

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Our work studies the effect of a pH-driven Li⁺-doping approach (Fig. 1a)) on the conductivity of polyelectrolyte multilayers (PEMs) containing poly(acrylic acid) (PAA). This approach involves the postpreparational treatment of PEMs in LiCl solutions at increased pH when compared to the pH of preparation. The goal is to compensate the resulting negative excess charge due to the deprotonation of PAA by the incorporation of Li⁺ ions.

The deprotonation of PAA inside poly(diallyldimethylammonium) (PDADMA)/PAA multilayers is successfully observed via *in-situ* Attenuated Total Reflection-FTIR (ATR-FTIR) studies during the doping process. The deprotonation is only seen for the treatments in LiCl solutions and does not occur in the case of pure water, which suggests Li⁺ ion uptake. Additional *in-situ* Dissipative Quartz Crystal Microbalance (QCM-D) experiments reveal slow equilibration processes lasting for up to 5 d, which involve losses in mass coverage.

Impedance spectroscopy studies are conducted according to a routine established by Akgöl *et al.*[1]. The DC conductivities, which were measured at 54 %RH, increase from $(12 \pm 1) \cdot 10^{-9}$ S/cm for as-prepared samples (pH 4) to $(7 \pm 1) \cdot 10^{-7}$ S/cm for samples treated in 0.1 M LiCl solutions at pH 7. A significant increase in the conductivity due to postpreparational treatments was hereby successfully proven (see Fig. 1).

Currently, ongoing studies investigate, to which extent the conductivity enhancement can be attributed to Li⁺ ions as charge carriers, or to possibly enhanced hydration accompanied by increased proton mobilities.

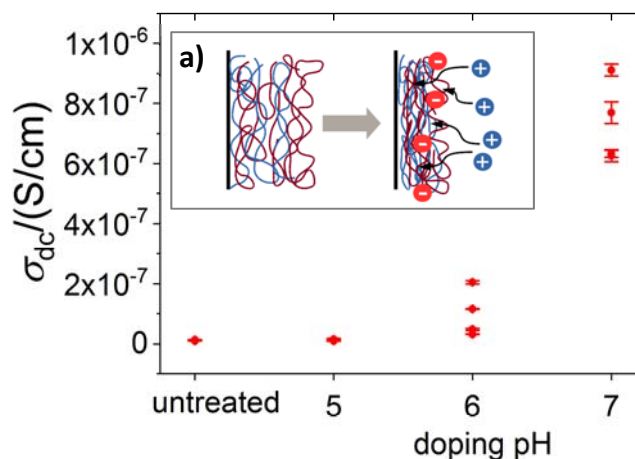


Figure 1. DC conductivity of (PDADMA/PAA)₅₀ PEMs prepared at pH 4 and treated in 0.1 M LiCl solutions at different pH values. Multiple samples were prepared for each pH. The error bars represent deviations determined for each sample, respectively. **a)** Scheme of the pH-driven approach of doping in LiCl solutions based on the generation of negative excess charges inside the PEM.

[1] Y. Akgöl, C. Hofmann, Y. Karatas, C. Cramer, H.-D. Wiemhöfer, M. Schönhoff, *The Journal of Physical Chemistry B* **2007**, 111, 8532-8539.