

**SELF-ASSEMBLED POLYELECTROLYTE COMPLEX COACERVATE
MEMBRANES FOR FLEXIBLE LOW-VOLTAGE ELECTRONICS**

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Reaction–diffusion (RD) plays a key role in natural structure-forming processes, including self-assembly and cell proliferation, which control the formation of a wide variety of structures, ranging from actin filaments, extracellular matrix to organs and skin patterns. Organic chemistry offers both an extremely wide range of chemical reactions and functional materials, as well as the possibility to precisely control chemical kinetics across multiple time scales, fabricate anisotropic structures and achieve spatial control over the formation of micro-objects by a polymerization reaction.

Mixing oppositely charged synthetic polyelectrolytes, which typically have higher charge densities than proteins, spontaneously yields a hydrated complex, or polyelectrolyte coacervate (PEC). It can have solid- or liquid-like properties. The morphology, stability, and properties of the latter strongly depends on its ion content, which moderates the reversible interactions between oppositely charged repeat units, providing the fascinating range of coacervate features to stimulate the interest in these amorphous viscoelastic materials. The layer-by-layer self-assembly technique enables the sequential deposition of ultrathin polyelectrolyte multilayer films driven by electrostatic interactions of oppositely charged polycations and polyanions, leading to the formation of radial concentric rings and tangential periodic bands, known as Liesegang structures. Despite the fact that significant progress has been made in the theoretical understanding of Liesegang phenomenon physicochemical mechanisms, the research of periodic precipitation in the application to polyelectrolyte spatiotemporal self-assembly remains limited.

The main objective of our research was to describe patterned supramolecular structures and the electrochemical properties of poly(ethyleneimine) (PEI) and poly-4-sodium-styrene-sulfonate (NaPSS) multilayer polyelectrolyte membranes. 1-% agarose gels doped with NH_4F and selected polyelectrolytes of various concentrations and average molar weights were employed as a medium to obtain the investigated membranes in two different setups: Petri dishes and tubes. Dissolved polycation and polyanion diffused towards each other to react at the crossing of the diffusional fronts and shape spatial concentration patterns, forming a supramolecular structure through layer-by-layer self-assembly. As a result, it has been observed that ranging polyelectrolyte concentrations and polymer molar weights significantly affects the speed of membrane formation, as well as the size and density of derived layered structures.

The integration of the obtained PEI — NaPSS self-assemble with eutectic gallium-indium eGaIn (75 wt% Ga, 25 wt% In) leads to the formation of a reconfigurable electronic component interface with the controllable system response, assessed by cyclic voltammetry (CV). A set of current-voltage characteristics was recorded on the source measure unit Keithley-6430 in two voltage ranges (250 mV and 750 mV) over the first 6 days of a multilayer PEI — NaPSS ($0.1M NH_4F$) film evolution and a month after membrane formation in the presence of $0.1M NH_4F$, $0.1M NaF$ and $0.1M NaCl$. Registered curves

confirm the formation of a proper diode component, exhibiting non-identical behaviour in dependence on the shape and ion content of the investigated self-assembly, which defines the thickness of an insoluble gallium compound layer between the electrode surface and the gel.

It has been experimentally revealed that the electrical behaviour of a multilayer polyelectrolyte film markedly differs from that of individual membrane components: PEI, NaPSS, NH_4F , as well as of an initially precipitated PEI — NaPSS ($0.1M NH_4F$) coacervate, distributed in the 1-% agarose gel. Thus, layer-by-layer self-assembly has been proven to enable the formation of various derivatives with the desirable properties of specificity, distinct geometry, charge characteristics and electrical behaviour.

In conclusion, the feature of periodic structures mimicking, as well as the exhibition of timely responses to tiny variations propel the development of advanced structure- and composition-controllable systems, like the investigated self-assembled PEI — NaPSS multilayer films, which may be subsequently integrated into sophisticated products to meet the demands of modern bioengineering and flexible electronics. The significant advantages over conventional electronic components include cheaper and more straightforward production processes, as well as a broad range of applications due to improved mechanical properties, deformability and electrical reconfigurability.