



# International Symposium on Polyelectrolytes

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## Polyelectrolyte interaction with redox-active counterions

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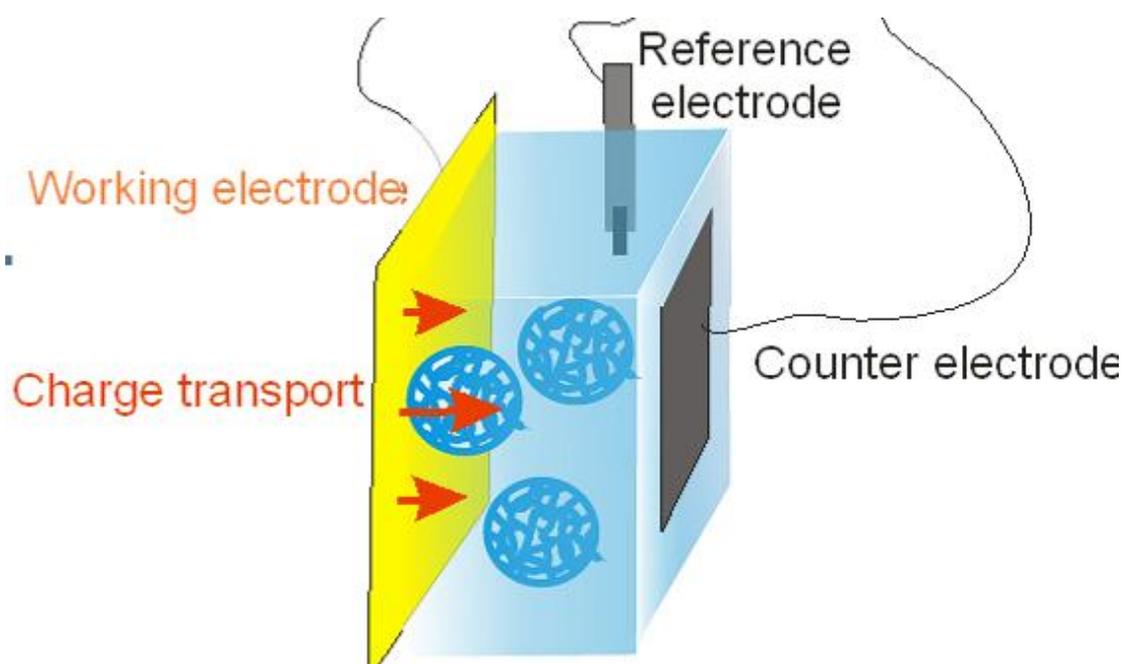
Polyelectrolytes interact strongly with multiple-charged counterions. This complexation is most pronounced for the interaction of oppositely charged macroions.[1] But also smaller, inorganic species can lead to complexation with charged polymeric species, while the charge of the inorganic coordination compounds can be changed by various means. Besides light-sensitive counterions,[2] electrochemically-addressable counterions are of scientific interest since years, going back to the seminal work of Anson et al. For example, electrolysis of complexes between polyelectrolytes and hexacyanoferrates lead to film formation onto the electrodes,[3] while the charge transport through the films is still facile.[4] At the same time, the polymer architecture has an influence on these processes. We could show recently that the use of branched bis-hydrophilic polymer structures together with the mobility of the redox-active species favours bulk aggregation instead of film formation on the electrode.[5] Simultaneously, the electrochemical switching of macromolecules between the unimeric and the micellar/vesicular state could be observed for the first time. We now address the influence of macromolecular structure on the electrochemistry of hexacyanoferrates by help of rotating ring disk electrode measurements. While linear cationic polyelectrolytes form conducting films at the electrode upon oxidation of ferrocyanide, charged microgels hardly adsorb on the electrode. Even more, our preliminary results counterintuitively indicate that the charge transport can be facilitated in presence of highly charged microgels. When diluting the charges on the microgel scaffold by copolymerization with a noncharged monomer, the charge transport is hindered in comparison to the hexacyanoferrate solution without polymer. These results indicate that microgels can have a modulating influence on the electrochemical properties of hexacyanoferrates.



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