Experimental report

06/10/2022

Proposal: **9-11-2050** **Council:** 4/2021

Title: Neutron scattering investigation of charged polymers dynamics for application in redox flow batteries for energy storage

Research area: Materials

This proposal is a resubmission of 9-11-2014

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Experimental team: Margarita RUSSINA

Local contacts: Ingo HOFFMANN
Lionel PORCAR

Samples: (D2C=C(CD3)CO2CD2CD2N(CD3)3Cl)m (C9D18NO)n
(N(CD3)3+)m(C9D18NO)n

Instrument	Requested days	Allocated days	From	To
D22	1	1	21/09/2021	22/09/2021
IN15	5	4	17/09/2021	21/09/2021

Abstract:

The major challenge in the integration of storage capacities in the existing electrical grid system is the development of durable and low cost solutions for energy storage, e.g. redox flow batteries (RFBs). The performance of RFBs depends to large extend on the charge transfer in electrolytes, connected to their viscosity and to diffusion/ relaxation processes at nanoscale. Here we propose to investigate nanoscale relaxation dynamics of organic copolymers, who are promising candidates for highly efficient organic electrolytes in RFBs applications. In our first study of cationic comonomer, whose structure consists from periodically distributed cation units, we observed charge-induced changes originating from the change of the polymer chains shapes and increased chains interactions. Now we would like to extend this study to zwitterionic polymers whose structure consists of oppositely charged cationic and anionic groups along the side chain with attractive and repulsive interactions. Beside the industrial interest, this gives an opportunity of the systematic study of cooperative ionic interaction and provide a fundamental understanding of the charge transfer at the nanoscale.

Charge induced conformational changes of organic materials in aqueous electrolytes for applications energy storage devices.

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Instruments: D22, D11, IN15.

Local contacts: Sylvain Prevost, Lionel PORCAR, Ingo Hoffmann

Motivation The major reason of the current storage capacities dearth is the cost, therefore the development of the *durable and low cost solutions for energy storage is of outmost importance.* Redox flow batteries (RFBs) enjoy a renaissance today due to their ability to store large amounts of electrical energy relatively cost-effective and efficient. The team of one of the project collaborator has recently developed aqueous, polymer based redox flow batteries, *which allow non-corrosive, safe and low cost operation by using organic polymers as the charge-storage material in combination with an aqueous sodium chloride solution as the liquid electrolyte*.

Results In our study in Sept 2021 we investigate the behavior of two very promising electrolytes, with a high potential for a high performance electrolyte application in RFBs. The first electrolyte uses cationic copolymers, whose structure consists from cation units distributed in a periodic way along the polymer structure with repulsive interactions. The second electrolyte is built from zwitterionic copolymers, with oppositely charged cationic and anionic groups along the side chains with attractive and repulsive interactions between monomer units present. In both electrolytes the REDOX unit responsible for charge is a well-known TEMPO copolymer. In the experiment, polymers were systematically charged, simulating the charging / discharging process in RFBs, when the charge of the redox moiety changes. Overall, the charge of the polymer chain will increase – from half of the repeating units are charged (SOC = 0%) to all repeating units are charged (SOC = 100%). In addition, we have investigated the influence of the TEMPO unit and ionic copolymer by modulating of the structure.

Investigation of the structure. The investigation of the structure has been conducted using D11 and D22 spectrometers at ILL. Fig. 1 shows the collected pattern from both type of the electrolyte with and without charge. The fitting of the data reveal that the charged polymers become more compact and spherical. Surprisingly, the increase of Tempo or ionic copolymers contributions does not have an impact on the structure shape and molecular size. Investigation of the dynamics have been conducted on neutron spine echo spectrometer IN15. The data show subtle differences in the dynamics as a function of charge, which were more pronounced for the zwitterionic samples. In all samples we observe a slow- down of the dynamics at Q ~ 0.06 $Å^{-1}$ (Fig.2). The more detailed analysis is currently underway.

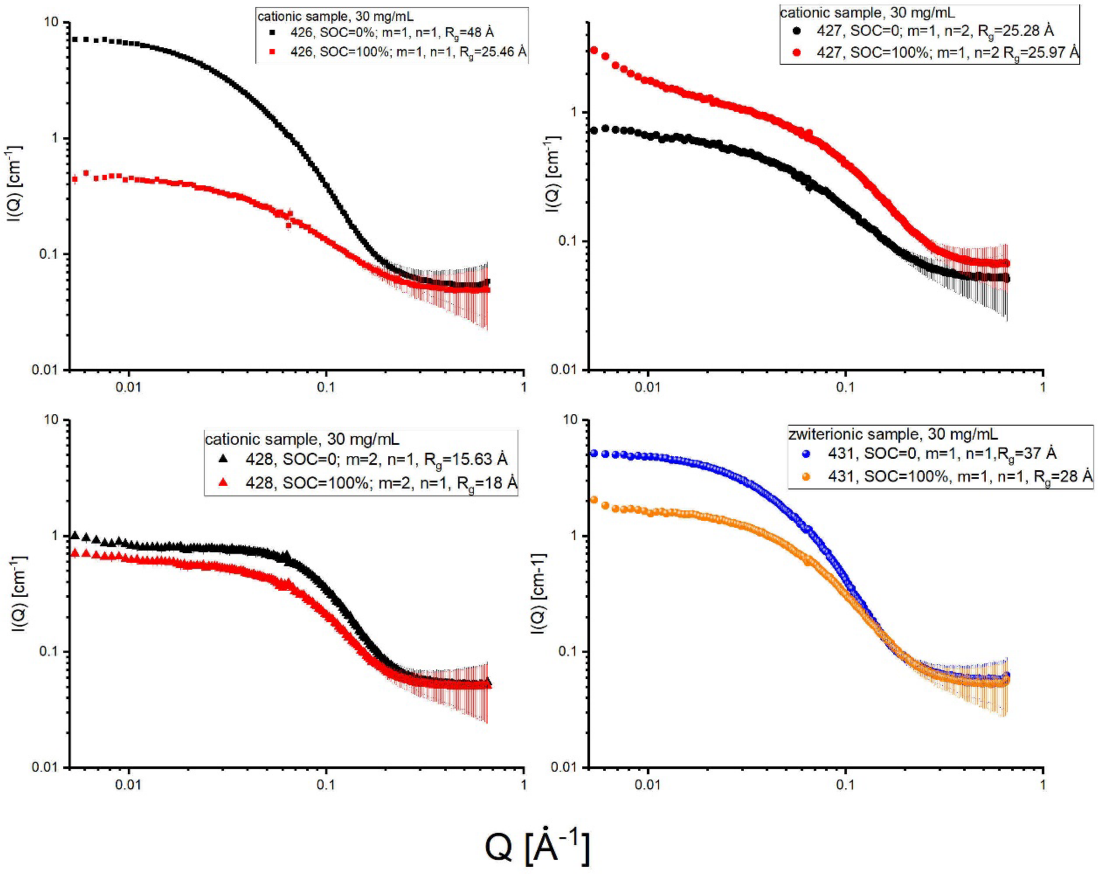

Figure 1 The SANS pattern for the samples with and without charge

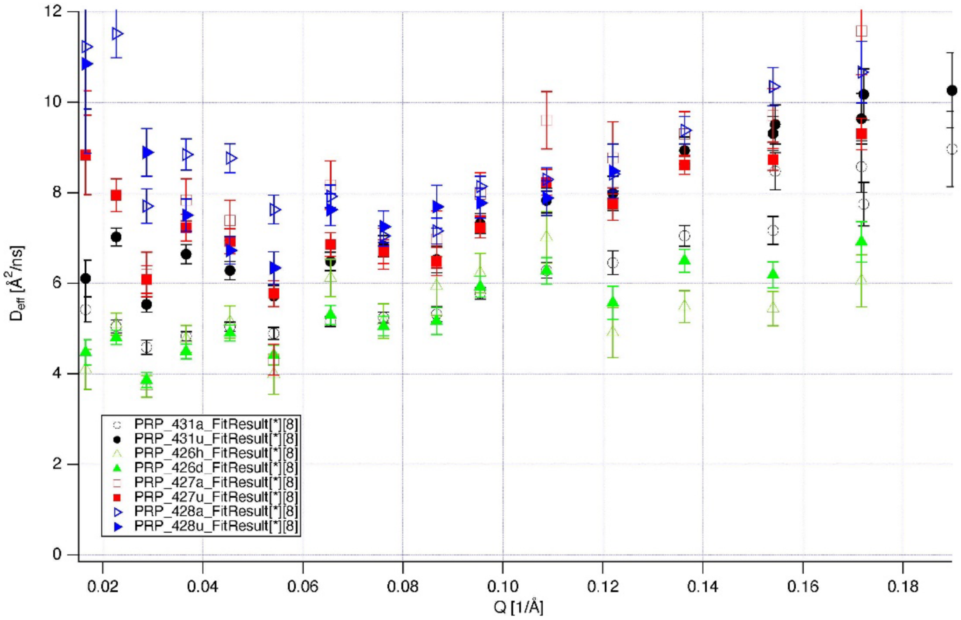

Figure 2. Calculated diffusion coefficient for the cationic samples (426, 427 and 428) and zwitterionic samples (431) with and without charge.