## **Supplementary Materials**

## Ion Conduction and its Activation in Hydrated Solid Polyelectrolyte Complexes

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- S1: (a) Influence of the relative humidity of the environment on the water content in  $x \operatorname{CsPSS}(1-x) \operatorname{PDADMAC}$  at ambient temperature.
  - (b) Water content of 0.55 MPSS · 0.45 PDADMAC PEC with Na<sup>+</sup> and Cs<sup>+</sup> ions, respectively. All straight lines have been calculated using Equation (1). In the case of PEC with NaPSS the proportionality factor is 0.230 ± 0.005, whereas it is 0.203 ± 0.003 for PEC with CsPSS.



S2: Temperature-dependent conductivity spectra of the cRH-series: (a) NaPEC and (b) CsPEC, both with MPSS = 0.60. At each temperature the samples were kept in an environment with 46% RH.



S3: Arrhenius plots of the PEC with MPSS from the cRH-series.
The data were taken at three different RH values, viz. 46%, 55% and 64%. Data for different compositions and types of alkali cations are shown: (a) x<sub>NaPSS</sub> = 0.55, (b) x<sub>CsPSS</sub> = 0.55, (c) x<sub>NaPSS</sub> = 0.60, (d) x<sub>CsPSS</sub> = 0.60.



S4: Master curves obtained by Summerfield scaling of the different isotherms displayed in Figure S2
(a) PEC with x<sub>NaPSS</sub> = 0.60 and (b) PEC with x<sub>CsPSS</sub> = 0.60. The samples were exposed to RH =

46% at each temperature (cRH-series).