

A zeolite crystallisation model confirmed by in-situ observation

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Supplementary information

1. Experimental Details

1.1 Sample preparation

Zeolite synthesis liquids were prepared based on a previously reported procedure for HSIL zeolite synthesis. As a source of silicate, two HSILs were made based on Na⁺ and Cs⁺. These will be referred to as the Na-HSIL and Cs-HSIL, respectively. The Na-HSIL is prepared by the hydrolysis of 1 TEOS (98%, ACROS Organics) : 1 NaOH (>97%, ACROS Organics) : 25 H₂O (Milli-Q) under mechanical rotation. After 24h, coacervation separates the mixture in an organic solution, containing water and the ethanol released by TEOS hydrolysis, and a dense ionic liquid, containing silicate oligomers, NaOH and a limited amount of water. Gravimetric analysis and NMR measurements indicate the ionic liquid phase, the Na-HSIL, has a composition of 1 Si(OH)₄ : 1 NaOH : 2.2 H₂O. Similarly, the alkaline hydrolysis of 1 TEOS (98%, ACROS Organics) : 1 CsOH (Sigma-Aldrich CsOH.H₂O >99.5% trace metal basis) : 10 H₂O (Milli-Q) yields an ionic liquid of composition 1 Si(OH)₄ : 1 CsOH : 2.3 H₂O. Zeolite synthesis liquids of 0.5 Si(OH)₄ : 0.03 Al(OH)₃ : 1 MOH : 5 H₂O were prepared with M = Na/Cs, following the same methodology. An alkaline solution is prepared by combining the appropriate amount of water with NaOH/CsOH. Once cooled down to room temperature, Al(OH)₃ added to the solution to and left to hydrolyse. Finally, the prepared Na-HSIL/Cs-HSIL is combined with the solution and stirred for 24h at room temperature. Once completed, the in-situ conductivity synthesis experiments performed at 60, 70, 80 and 90°C. From the identical zeolite synthesis liquid batch, these syntheses are ex-situ replicated by hydrothermal

treatment of PP vessels (Oak Ridge™, Fischer Scientific), filled with 25.00g of zeolite synthesis liquid, at 60, 70, 80 and 90°C for a synthesis time as provided in Table. S1

1.2 In-situ MEEIS synthesis experiment

During zeolite synthesis, monophasic HSIL synthesis liquids turn into 2-phasic systems, containing significant amounts of zeolite crystals, potentially sedimenting. Conventional 2- or 4-electrode conductometry is unable to discriminate between liquid or solid fractions, preventing the exclusive measurement of the synthesis liquid conductivity for sedimenting systems³⁴. Therefore, a new conductivity measurement methodology was developed, moving electrode electrochemical impedance spectroscopy (MEEIS). MEEIS is capable of high-accuracy conductivity measurement of dynamic systems, including particle sedimentation or electrode corrosion^{33,34}. In short, MEEIS utilizes a moveable electrode with adjustable electrode distance between two opposing, vertically arranged electrodes (Fig. S1). By recording impedance spectra at different electrode positions, the conductivity can be determined by a modified version of Pouillet's law,

$$\sigma = \frac{1}{a A},$$

with a the impedance increase per unit electrode distance and A the cross section of the sample tube. Practically, a is determined by line fitting through the impedance values as a function of the electrode distance. For electrode sensors with a static design, the impedance of liquid samples depends on the frequency of the applied AC signal, making the choice of the measurement frequency crucial to determine conductivity correctly (Fig. S2). Using MEEIS, however, constant contributions to the impedance, such as the inductance of wires, long-term passivation of electrodes and the double layer effect, are eliminated³³. This makes this

technique ideally suited to all kinds of corrosive and highly ionic samples, such as zeolite synthesis media (Fig. S2, Fig. S3).

1.3 Fitting of the conductivity growth model

The MEEIS recorded conductivity curves were fitted with the crystallisation kinetics conductivity model,

$$P_{crystal}(t) = \frac{\text{fraction of total solid aluminosilicate}}{\text{total solid aluminosilicate}} \propto \frac{\sigma(t) - \sigma(t_0)}{\sigma(t_{final}) - \sigma(t_0)}$$

Where the probability for charge release is given by,

$$P_N(t) = 1 - \exp[-G t^z]$$

As the crystallisation model is formulated as an expression of $\sigma(t_{final})$ and $\sigma(t_0)$, these must be included as parameters in the fitting function. Therefore, the conductivity curves were fitted with the model,

$$\sigma(t) = A + B (1 - \exp[-G t^z]),$$

employing the least squares curve fitting function of the `scipy.optimize` package in Python 3.

1.4 CrystalGrower simulations

The CrystalGrower simulations were performed at a simulation temperature of 90°C for 1.000.000 iterations. Supersaturation profile 3 was found to be most realistic compared to the in-situ observed kinetics of crystallisation. To limit the explicit simulation influence of supersaturation, a high and constant supersaturation of $\Delta\mu_1 = 50$ kcal/mol was chosen with supersaturation parameters of $I_1 = 200000$ and $\Delta I_e = 600000$. The simulations were performed for equal Q_n and tile scaling. The baseline energy separation was varied between value of 0, 0.25, 0.40, 1.0 and 2.0 kcal/mol. Simulations were also performed using different saturation profiles to ensure that the observed baseline energy separation dependent formation is not related the usage of a specific supersaturation profile.

2. Supplemental Figures

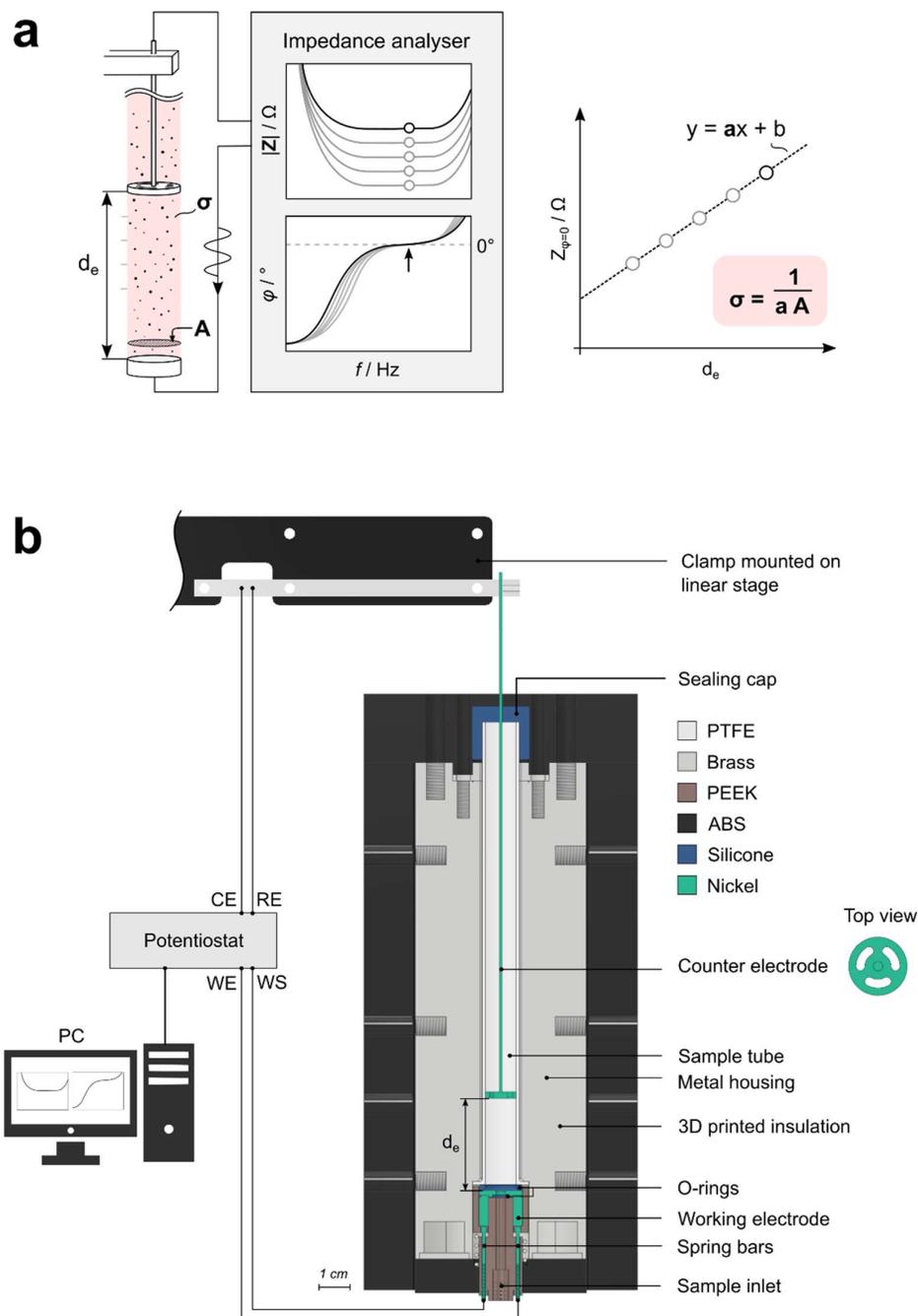


Fig. S1 Moving electrode electrochemical impedance spectroscopy (MEEIS).a, Overview of the MEEIS measurement principle. Conductivity measurements are performed at multiple interelectrode distances for a spectrum of measurement frequencies. Based on the frequency spectrum, a measurement frequency is chosen based on the impedance phase angle, yielding the real contribution to the impedance if $\text{Arg}(Z) = 0^\circ$. In this case, the slope of the electrode distance vs measured solution resistance curve yields the solution conductivity. b, Overview of the experimental set-up.

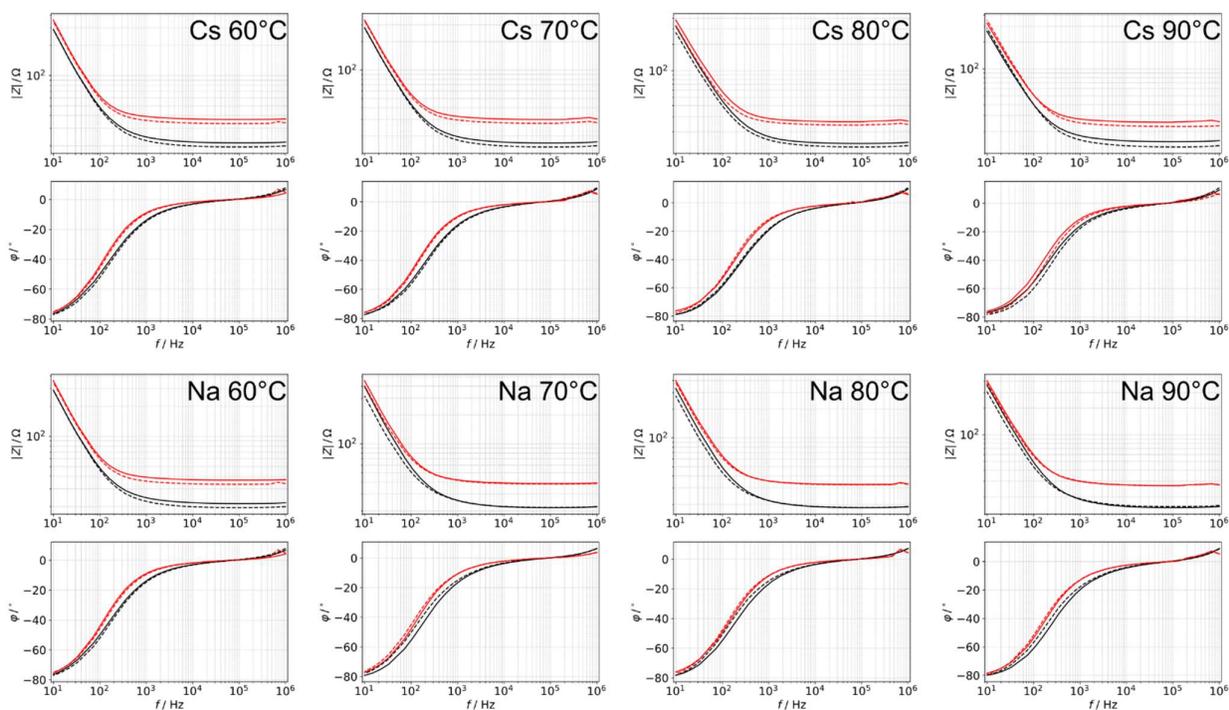


Fig. S2 Overview of recorded impedance spectra. The impedance recorded at the start (solid line) and the end (dashed) of in-situ measurement for interelectrode distances of $d_e = 5\text{cm}$ and $d_e = 9\text{cm}$ are given by black and red lines, respectively.

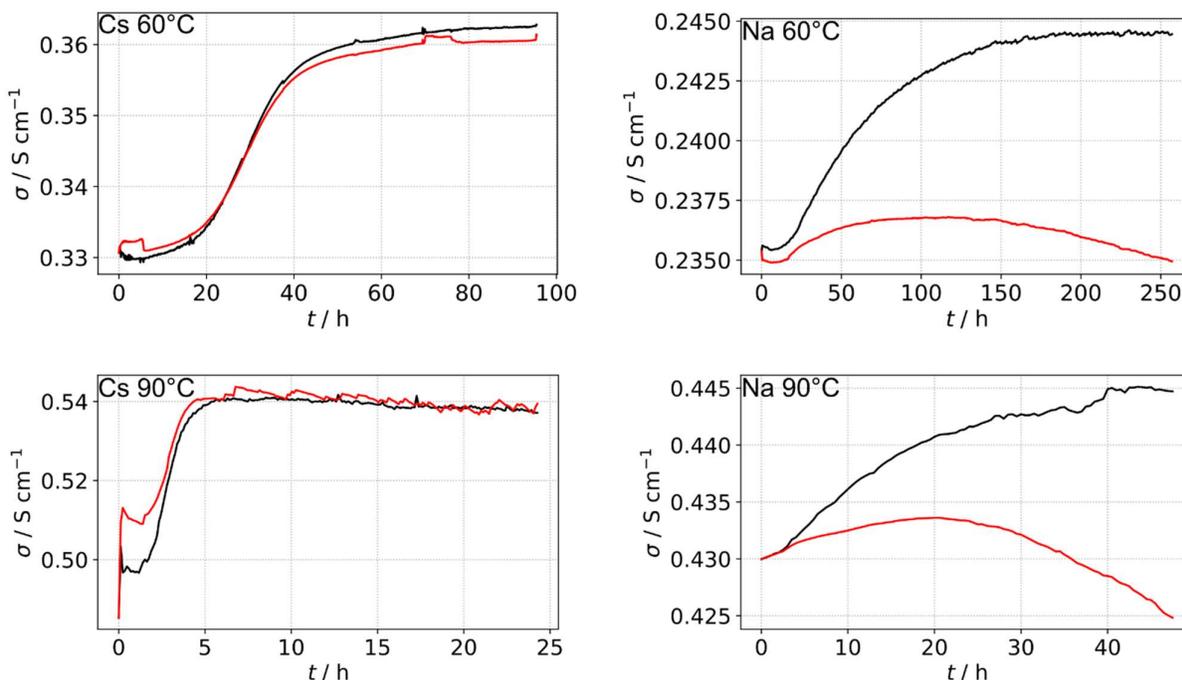


Fig. S4 Comparison of MEEIS conductivity data based on a fixed interelectrode distance (red) or conductivity determination via measurement at multiple interelectrode distances via Pouillet's law (black).

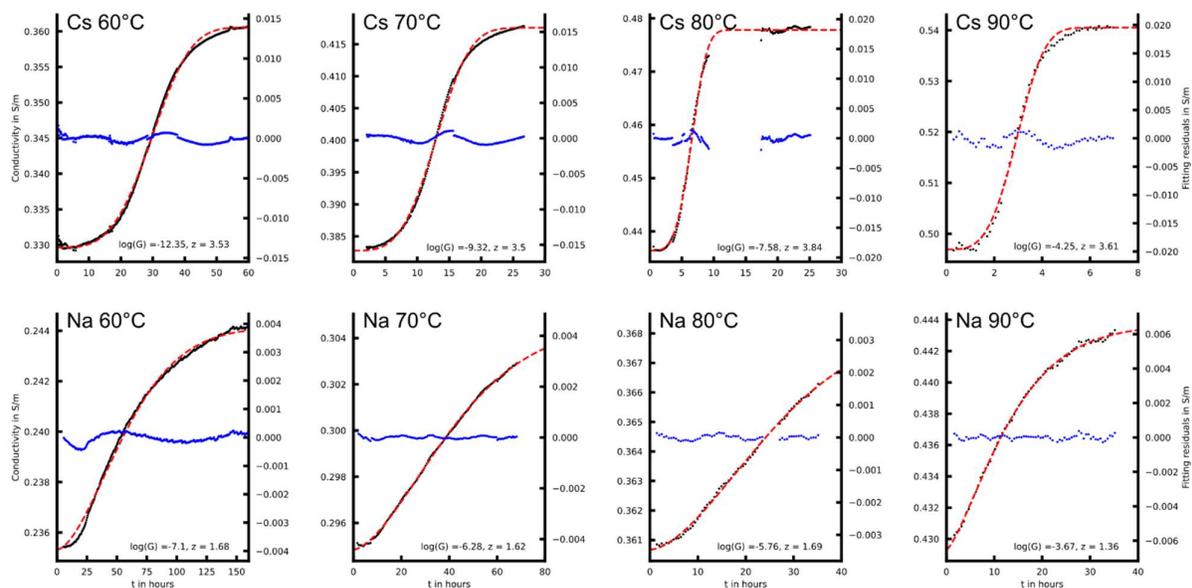


Fig. S4 Overview of the measured conductivity curves (black dots) including the model fit (dashed red line) and the fitting residuals (blue dots)

3. Supplemental tables

Table S1 Employed synthesis timings for ex-situ zeolite synthesis replication

Sample	Synthesis time (h)
Na 60°C	97.0
Na 70°C	60.7
Na 80°C	57.1
Na 90°C	20.7
Cs 60°C	41.5
Cs 70°C	17.6
Cs 80°C	8.6
Cs 90°C	4.0

Table S2 Measured conductivity data for zeolite synthesis liquids containing Na⁺ or Cs⁺ cations at the employed synthesis temperatures, before (σ_{t_0}) and after synthesis ($\sigma_{t_{end}}$).

$T_{syn}(^{\circ}C)$	$\sigma_{t_0}(S/m)$		$\sigma_{t_{end}}(S/m)$		σ_{Na}/σ_{Cs}	
	Na	Cs	Na	Cs	t_0	t_{end}
60	0.235	0.330	0.244	0.361	0.71	0.69
70	0.295	0.383	0.305	0.418	0.77	0.73
80	0.361	0.436	0.368	0.478	0.83	0.77
90	0.429	0.497	0.444	0.541	0.86	0.82