

Supplementary Information

Selective Li Ion Transport via Interpenetrated Crystal Growth on ZIF-8 Seeded Nanocomposite Membranes

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Experimental Procedures

Materials and Instruments: All chemicals were purchased from Sigma-Aldrich, TCI or Ambeed and used without additional purification. Electrochemical measurements were performed on a Biologic VSP-300 potentiostat using an electrochemical H-cell. Powder X-ray diffraction patterns (PXRD) were measured on a Bruker D8 Quest X-ray diffractometer and field emission scanning electron microscopy (FESEM) images were taken on a JEOL JSM-7401F. Cross sectional SEM and EDS mapping images were taken on a Hitachi SU3500 VP SEM. Surface images of MMMs were obtained on a Hitachi TM-4000PlusE-2. Fourier-transform infrared (FTIR) spectra were obtained on a Cary 630 ATR FT-IR spectrophotometer. Brunauer-Emmet-Teller (BET) surface area and NLDFT pore size distribution were measured with a Micromeritics ASAP 2020 PLUS porosimeter. Proton nuclear magnetic resonance (^1H NMR) was obtained with a Bruker Avance-III 300 NMR Spectrometer. Contact angles images were obtained on a Ramé Hart Model 250 contact angle goniometer.

Preparation of (nanocrystalline) ZIF-8: Nanocrystalline ZIF-8 was synthesized according to literature procedure with modifications to the reaction time and stirring parameters.^(S1) In a round-bottom flask, zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), (2.00 g; 6.72 mmol; 1.0 eq.) was dissolved in methanol (75 mL; 275 eq.) and set to stir at 300 rpm. In a separate flask, 2-methylimidazole (2mlm), (4.44 g; 54.08 mmol; 8.05 eq.) was dissolved in methanol (75 mL; 3708 mmol; 275 eq.). The 2-methylimidazole methanolic solution was quickly transferred to the round-bottom flask and left to stir at 300 rpm for 1 hour. A milky white suspension persisted after 5-10 minutes of reaction. The white powder was isolated by centrifugation (6000 rpm; 10 minutes) and washed three times with methanol. The powder was dried *in vacuo* (0.67 atm, 1 hour), and stored for further use.

Composition of PVDF and ZIF-8: The nanocomposite fabrication of 5s-MMM was guided by literature procedures.^(S2,S3) Poly(vinylidene)difluoride (PVDF, $n=1,100,000$; 354 mg) was dissolved in 1 mL of DMF at 85 °C with stirring to generate a 25 wt% solution. In a medium vial, the nanocrystalline ZIF-8 (19.2 mg), was suspended in acetone (3 mL) and sonicated for 30 minutes. The milky suspension was slowly added to the viscous clear PVDF putty at 85 °C with stirring. The viscosity notably reduced, and the acetone was left to boil off for approximately 1 hour with continued stirring. The resulting thick white paste was transferred to a stenciled glass slide, 250 μm indent, and blade coated. The gelatinous translucent membrane was left to thermally phase invert and outgas residual solvent overnight. The pristine white 5s-MMM was removed from the glass substrate via razor blade, and if necessary, deionized water was used to delaminate the surface from the glass. The 5s-MMM samples were stored in a dry environment, protected from UV light for further use.

Membrane Crystallization of ZIF-8 (5c-MMM): Crystallization parameters were adopted and modified from ZIF-8 crystallizations leveraging surface functionalized matrices and supports.^(S4) The 5s-MMM was prepared by immersing in 0.25 M methanolic $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution overnight. To a glass vial, sodium formate (156 mg; 2.3 mmol; 1.0 eq.) was dissolved in 7 mL of methanol and heated to 85 °C for 3 hours. Then, the 5s-MMM was transferred from 0.25 M methanolic

Zn(NO₃)₂·6H₂O solution to the hot formate solution. Zn(NO₃)₂·6H₂O (677 mg; 2.3 mmol; 1.0 eq.) was dissolved in 4 mL of methanol and added to the membrane containing reaction vial. Next, 2-methylimidazole (385 mg; 4.69 mmol; 2.0 eq.), was dissolved in 4 mL of methanol and added to the reaction vial. The Teflon capped vial is sealed tightly, and the crystallization was allowed to proceed for 16 hours unstirred. After exhaustion of the reaction, 16 hours, the vial resembled a *snow-globe* and the membrane were removed with tweezers and left to soak in methanol for 1 hour. The membrane was transferred to 1:1 methanol-water solution for 4 hours, and finally immersed in DI water overnight. The membranes were then removed from the wash bath and allowed to dry on a glass slide under ambient conditions, followed by thickness measurement with a caliper, and storage in a dry environment protected from UV light, for further use.

Truncated Membrane Crystallization of ZIF-8 (5c-MMM-4h): Truncated crystallizations were performed identical to the procedure outlined in **Membrane Crystallization of ZIF-8 (5c-MMM)**, however, the MMMs were removed from the reaction vial after 4 hours.

¹H NMR digestion: The respective compositions of the 5s-MMM and 5c-MMM were characterized by digested ¹H NMR. Samples were prepared by dissolving the polymer matrix in d₆-DMSO with thorough sonication for 1 hour. The suspension was then subjected to acid to digest the ZIF-8 and free its respective 2-methylimidazole. For 5s samples, 10% v/v DCI in D₂O sufficed as only 2-3 drops were typically necessary. For the 5c-MMM, neat HNO₃ was used alternatively as more acid was required to fully digest the MOF, while the added D₂O from 10% v/v DCI in D₂O can lead to the precipitation of PVDF. Quantitative estimates to the ZIF-8 composition were performed by analyzing the observed aromatic proton integrations of 2-methylimidazole (in ML₂: 4H) and PVDF (2H) and mass resolving them to their respective unit mass/molar masses.

$$(1) [2mlm Ar(H)] \cdot \left(\frac{277.4771g}{mol} \right) \cdot \left(\frac{2H}{4H} \right)$$

$$(2) [PVDF HT(H) + HH(H)] \cdot \left(\frac{63.034g}{unit} \right)$$

Equations S1 and S2. Mass resolution of both ZIF-8 (1) and PVDF (2) to ¹H NMR integration in compositional analysis. HT and HH refer to ¹H NMR signals arising from head-tail and head-head configurations respectively; Ar(H) refers to the aromatic protons of 2-methylimidazole (2mlm).

The mass resolved integration was then used to generate a quantitative estimate to the total composition assuming all 2-methylimidazole derived a defect-free ZIF-8 structure, no deprotonation of the chemically resistant PVDF, and the total mass of the composite membrane was comprised solely of the ZIF-8 and PVDF.

$$(3) \frac{[ZIF - 8 Ar(H)]}{[ZIF - 8 Ar(H)] + [PVDF HT(H) + HH(H)]}$$

Equation S3. Estimated membrane composition by digested ^1H NMR, assuming all 2-methylimidazole (2mlm) derived a defect-free ZIF-8 structure, and the total composition of the membranes are defined only by the ZIF-8 and PVDF.

Preparation of MMM for Transport Evaluation: 5s-MMM and PVDF membranes were prepared analogously to the 5c-MMM. The 5c-MMM was preconditioned using high vacuum (0.2 atm, 1 hour) to remove any residual solvents from the composition or crystallization reactions. The 5c-MMM was then fitted into an H-cell, with a 0.5 cm diameter opening defined as the active area of the MMM. The MMM was sandwiched between two Nafion O-rings and gently sealed between the chambers using a clamp. The seal was tightened thoroughly, and the chambers were filled with MilliQ water. Linear sweep voltammetry (LSV) sweeps were performed for several hours to ensure a stable system has been achieved and that no redox active sodium formate remains in the MMM to diffuse and contaminate ion transport measurements. Once a stable conductivity reading was established in MilliQ water, the MMM was conditioned for ion transport measurements.

Preparation and Evaluation of Electrolyte for Ion Transport: Alkali chloride electrolyte was constructed at 0.1 M concentrations, diluting with MilliQ water. All alkali chloride salts were obtained from TCI and used without further purification. Alkali salts were massed and volumetric glassware, 100 mL, was used to construct 0.1 M electrolyte solutions. Electrolyte dependent conductivities were evaluated to adjust for limiting ion identity dependent conductivities, as LiCl, NaCl, and KCl exhibited distinct current response at a given, 0.1 M, concentration.

Electrode Configuration and Geometry of H-Cell Ion Transport: To evaluate the ion identity dependent transport of the 5c-MMM, a concentration gradient was established across the H-cell by filling one chamber, *the concentrate*, with 0.1 M electrolyte solution, and the complementary chamber, *the diluate*, with MilliQ water. A two-electrode configuration of Ag/AgCl (1 M KCl) electrodes were leveraged to study the ion transport via LSV. The electrode geometry was defined by *working the diluate*, wherein the un-shortened working electrode stack (WE) drove the voltage gradient from the *diluate* chamber, while the shorted counter/reference stack (CE/RE) was placed in the *concentrate* chamber.

Ion Transport Evaluation of 5c-MMM via LSV-OCV: The ion transport properties of the 5c-MMM were evaluated by monitoring the decay of the OCV with the mass transport limited concentration gradient equilibration of the system. Linear sweep voltammetry was synchronized to the open circuit voltage measurement to observe the time dependent ion conductance of the system. Sweeping at 25 mVs^{-1} , over a potential range of -100 mV to 100 mV referenced against the Ag/AgCl (1 M KCl). The ion conductance was determined using Ohm's Law of the fitted linear slope of the voltammogram, and further, the ion conductivity was extrapolated with normalization to the geometry and thickness of the 5c-MMM. The resulting ion conductivities were then adjusted to their respective aqueous ion mobility dependence, measured experimentally (see Preparation and Evaluation of Electrolyte for Ion Transport). To do this, the extrapolated ion conductivities were multiplied by the ratio of limiting ion currents (Li/M) at 0.1 M in MilliQ water. Ion transport

evaluation of the 5s-MMM and PVDF membrane were performed analogously with the exclusion of a concentration gradient, as the resulting current responses were too low to analyze.

Water Uptake Experiments: Membrane samples were prepared by cutting into similar size rectangles, 0.5 x 1 cm, followed by drying under high vacuum, 0.2 atm, for 3 hours. The membrane samples were massed three times on an analytical balance and averaged to obtain a quantitative initial mass. The membranes were submerged in separated vials each containing 10 mL of MilliQ water. The vials were left undisturbed for 48 hours at room temperature. Upon 48 hours, the membranes were removed from their respective vials, the surface of the sample was dried with a Kim wipe, and the sample was massed three times again and averaged to obtain a quantitative final mass. The samples were removed and massed sequentially to mitigate effects of inconsistent drying time of the hydrophobic surfaces. The water uptake was determined by the mass change (wt.%) over 48-hour immersion in water.

Contact Angle Measurements: Contact angle measurements were performed to provide a qualitative assessment of the relative membrane surface hydrophobicity. Contact angles were recorded on a Ramé Hart Model 250. To prepare the membrane samples and remove any residual solvent or volatile contaminants from the surface, they were subjected to high vacuum, 0.2 atm for 1 hour. The membranes were then placed on a glass stage and water droplets, 10 μ L, were carefully placed on the top surface of the membranes; contact angle measurements were obtained by averaging the recorded value of ten images.

Results and Discussion

1) Additional Characterizations

Structural characterizations of ZIF-8

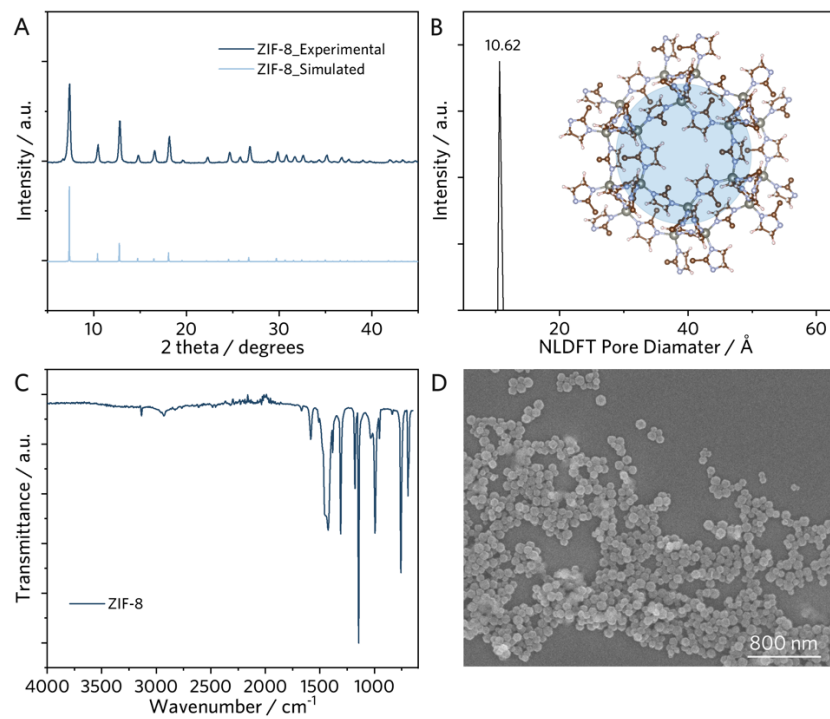
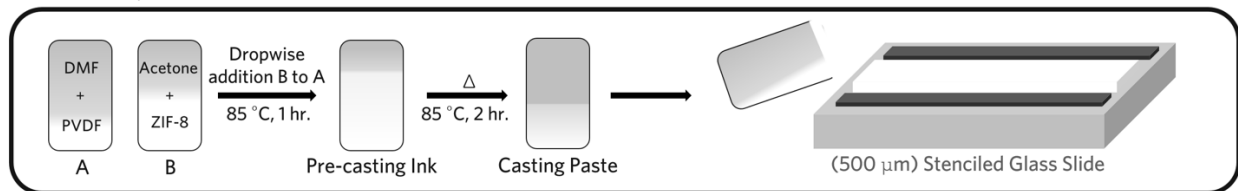


Fig. S1 (A) PXRD, (B) NLDFT pore size distribution, (C) FTIR, and (D) SEM image of nanocrystalline ZIF-8.

Synthetic scheme of 5s-MMM

A. Composite MMM Fabrication



B. Composite MMM Crystallization

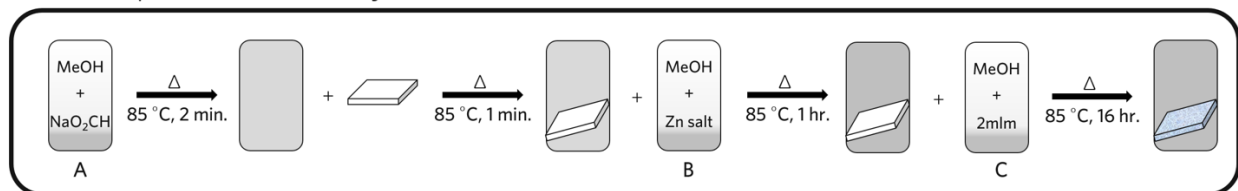


Fig. S2 (A) Fabrication scheme by solution state mixing (left) followed by thermal phase inversion at room temperature (right) of PVDF-nanocomposites, 5s-MMMs. (B) Schematic of the sodium formate modulated ZIF-8 crystallization of the 5s-MMM.

¹H NMR digestion

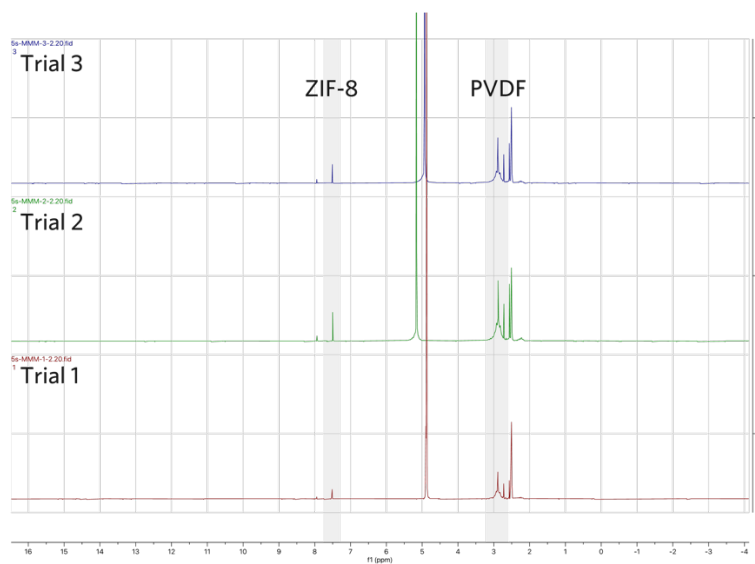


Fig. S3 ¹H NMR of 5s-MMM suspended in d₆-DMSO and digested with 10% v/v DCI in D₂O.

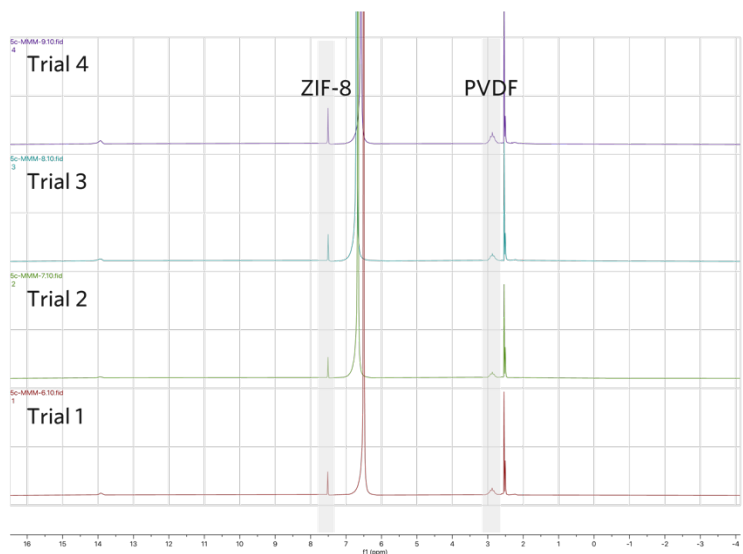


Fig. S4 ^1H NMR of 5c-MMM suspended in d_6 -DMSO and digested with *cat.* HNO_3 .

| Mass Resolved | 2mlm (Int. Ar(H)) | Mass Resolved (ZIF-8)* | PVDF (Int. $(\text{CH}_2)_n$) | Mass Resolved (PVDF)# | ZIF-8 (wt. %) ^{##} |
|---------------|-------------------|------------------------|--------------------------------|-----------------------|-----------------------------|
| 5s-MMM | 1.00 | 227.477 | 24.47 ± 2.7 | 1556.910 | 6.77 ± 0.7 |
| 5c-MMM | 1.00 | 227.477 | 3.04 ± 0.4 | 194.663 | 36.88 ± 2.65 |

Table S1. Digested ^1H NMR mass resolved compositional analysis. Int. means integration of each signal from digested ^1H NMR. *# Calculated by following Equation S1 and S2 in ^1H NMR digestion section. ## Calculated by following Equation S3 in ^1H NMR digestion section.

Water uptake experiment

| PVDF | Avg. mass (initial; mg) | Avg. mass (final; mg) | % mass change | Avg. % mass change |
|------|-------------------------|-----------------------|---------------|--------------------|
| 1 | 32.87 | 33.07 | 0.6% | 0.8 ± 0.4% |
| 2 | 22.40 | 22.70 | 1.3% | |
| 3 | 22.07 | 22.20 | 0.6% | |

Table S2. Summary of water uptake measurements for PVDF.

| 5s-MMM | Avg. mass (initial; mg) | Avg. mass (final; mg) | % mass change | Avg. % mass change |
|--------|-------------------------|-----------------------|---------------|--------------------|
| 1 | 37.20 | 39.87 | 7.2% | 5.4 ± 1.6% |
| 2 | 39.40 | 40.97 | 4.0% | |
| 3 | 38.03 | 39.93 | 5.0% | |

Table S3. Summary of water uptake measurements for 5s-MMM.

| 5c-MMM | Avg. mass (initial: mg) | Avg. mass (final: mg) | % mass change | Avg. % mass change |
|--------|-------------------------|-----------------------|---------------|--------------------|
| 1 | 49.63 | 60.97 | 22.8% | 29.2 ± 3.2% |
| 2 | 27.50 | 34.57 | 25.7% | |
| 3 | 26.30 | 34.73 | 32.1% | |
| 4 | 23.77 | 30.87 | 29.9% | |

Table S4. Summary of water uptake measurements for 5c-MMM.

3) Electrochemical Analysis

H-cell Image

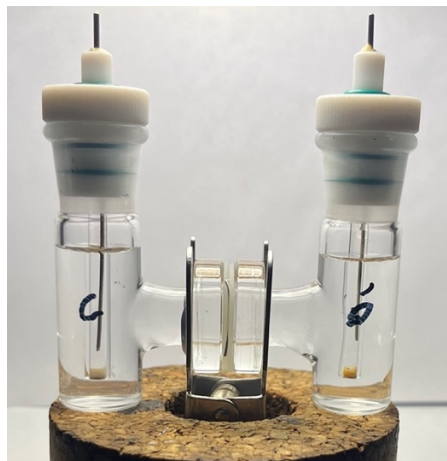


Fig. S5 Electrochemical H-Cell.

Linear sweep voltammetry

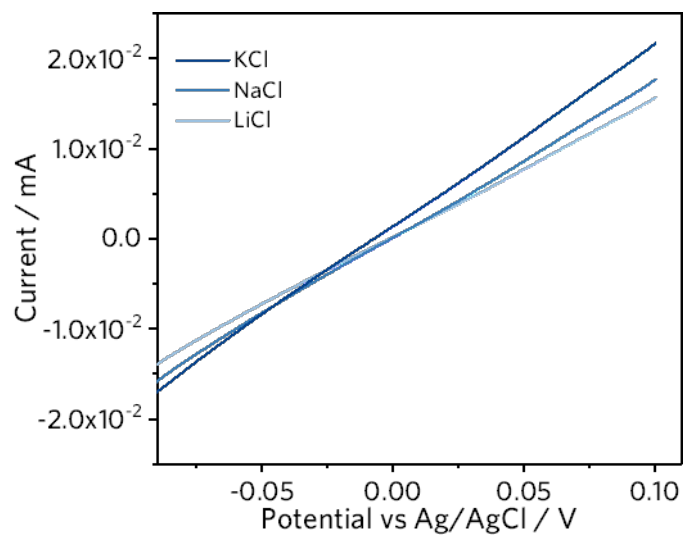


Fig. S6 LSV curves of blank electrolyte, obtained in an H-cell with a symmetric two-electrode configuration of Ag/AgCl (1 M) electrodes. Sweeps were recorded at 25 mV s⁻¹ in 0.1 M MCl (M = Li, Na, K).

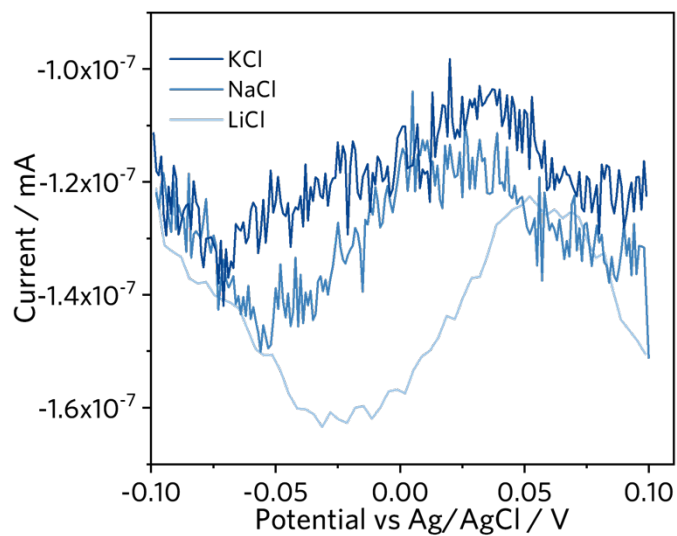


Fig. S7 LSV curves of PVDF obtained in an H-cell with a symmetric two-electrode configuration of Ag/AgCl (1 M) electrodes. Sweeps were recorded at 25 mV s^{-1} .

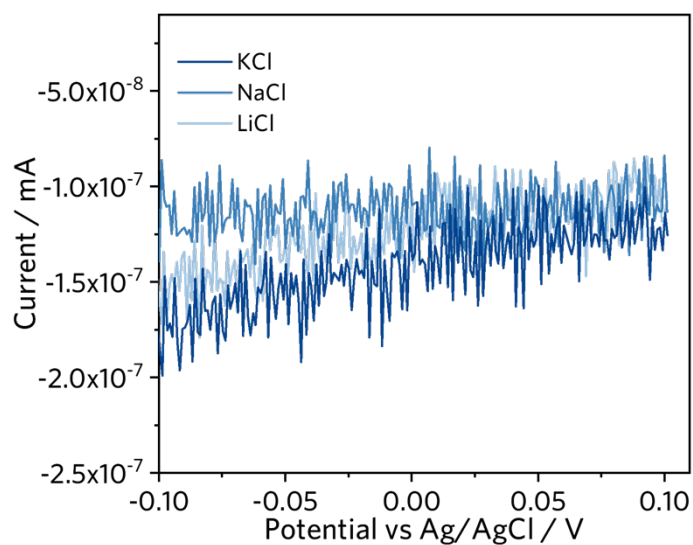


Fig. S8 LSV curves 5s-MMM obtained in an H-cell with a symmetric two-electrode configuration of Ag/AgCl (1 M) electrodes. Sweeps were recorded at 25 mV s^{-1} .

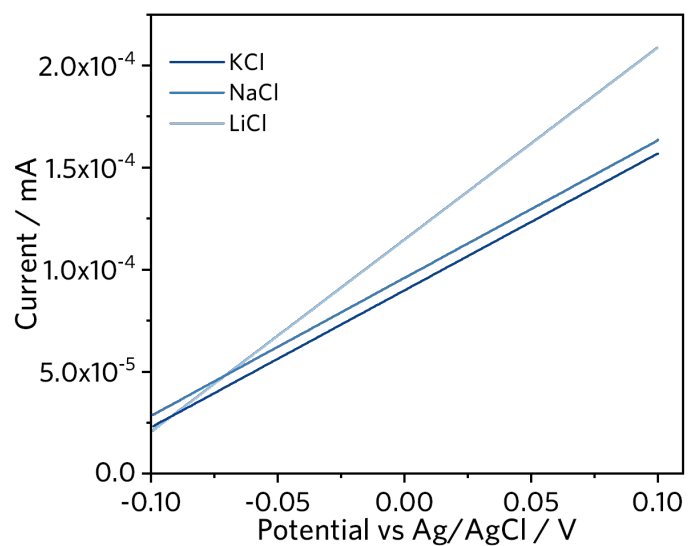


Fig. S9 LSV curves 5c-MMM obtained in an H-cell with a symmetric two-electrode configuration of Ag/AgCl (1 M) electrodes. Sweeps were recorded at 25 mVs^{-1} .

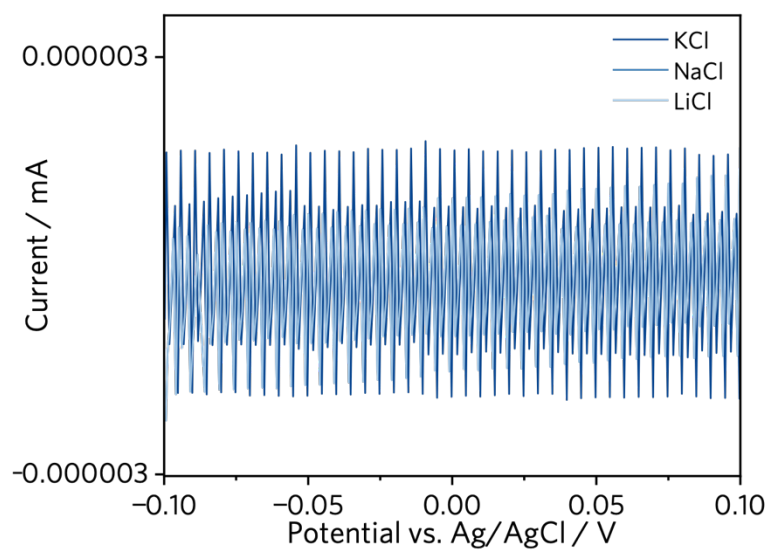


Fig. S10 LSV curves of 5c-MMM with a truncated crystallization (5c-MMM-4h).

Open circuit voltage

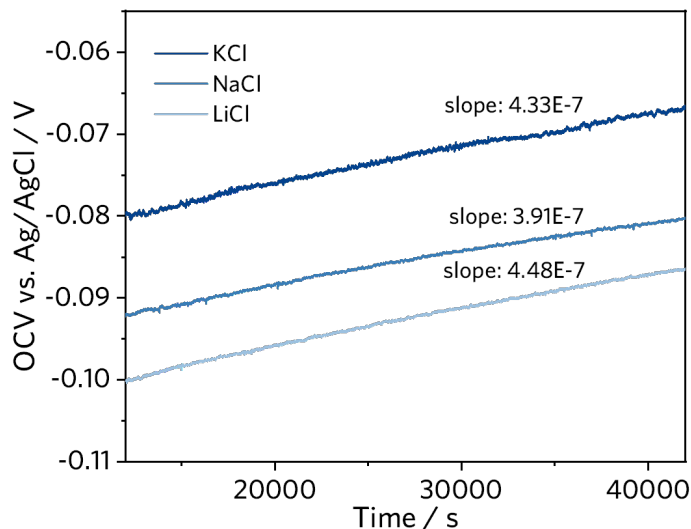


Fig. S11 OCV decay of 5c-MMM obtained in an H-cell and measured with symmetric two electrode configuration of Ag/AgCl (1 M), and asymmetric electrolyte configuration of 0.1 M gradient.

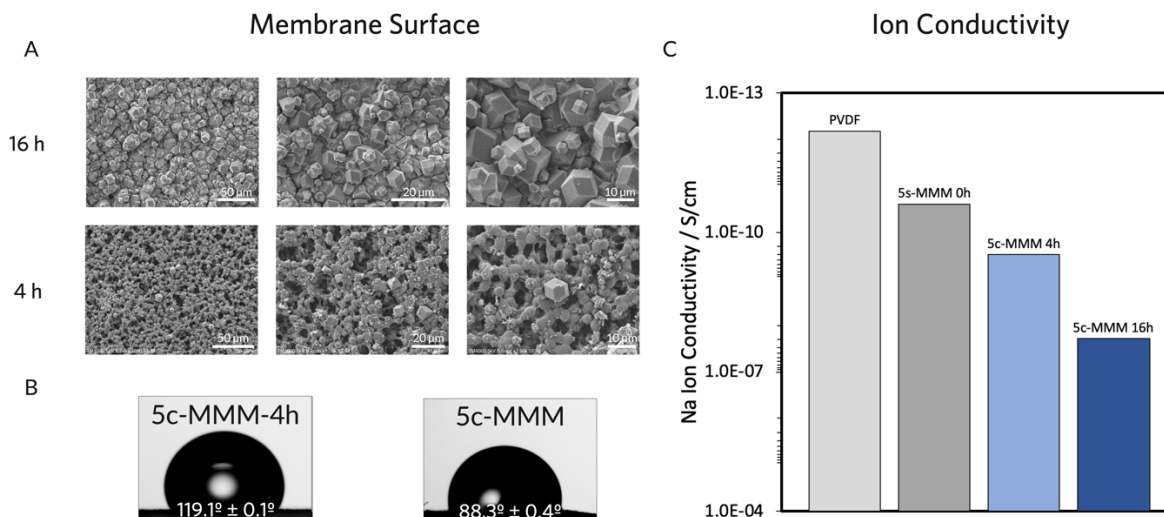


Fig. S12 (A) SEM images of time dependent ZIF-8 crystallizations of the 5s MMM. (B) Water contact angles of 5c-MMM-4h (Left), and of 5c-MMM (Right). (C) Ion conductivity measurements of PVDF, 5s-MMM, 5c-MMM-4h, and 5c-MMM-16h, obtained after a 12 hour diffusion period in an H-cell of 0.1 M gradient.

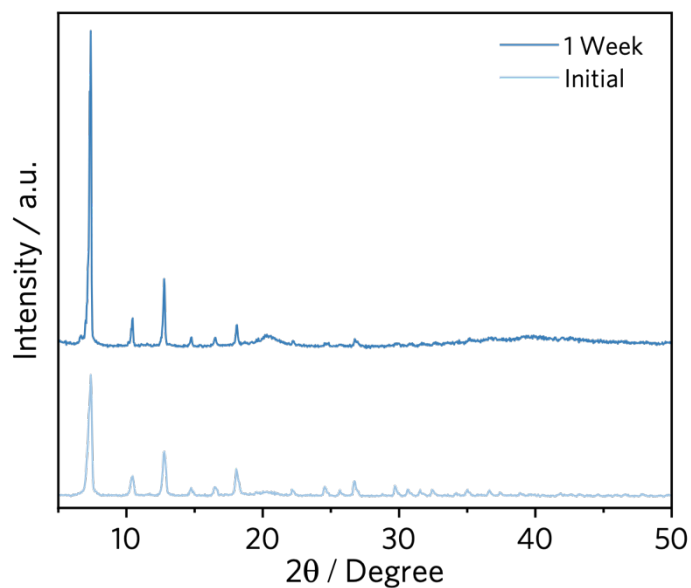


Fig. S13 Powder x-ray diffraction patterns of 5c-MMM samples before and after immersion in MilliQ water for 1 week, highlighting the retention of the ZIF-8 crystal structure in aqueous environment.

References

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