Supporting information:

**Corrosion stability of NASICON-based membranes against aqueous solutions: case study for sodium iodine batteries**

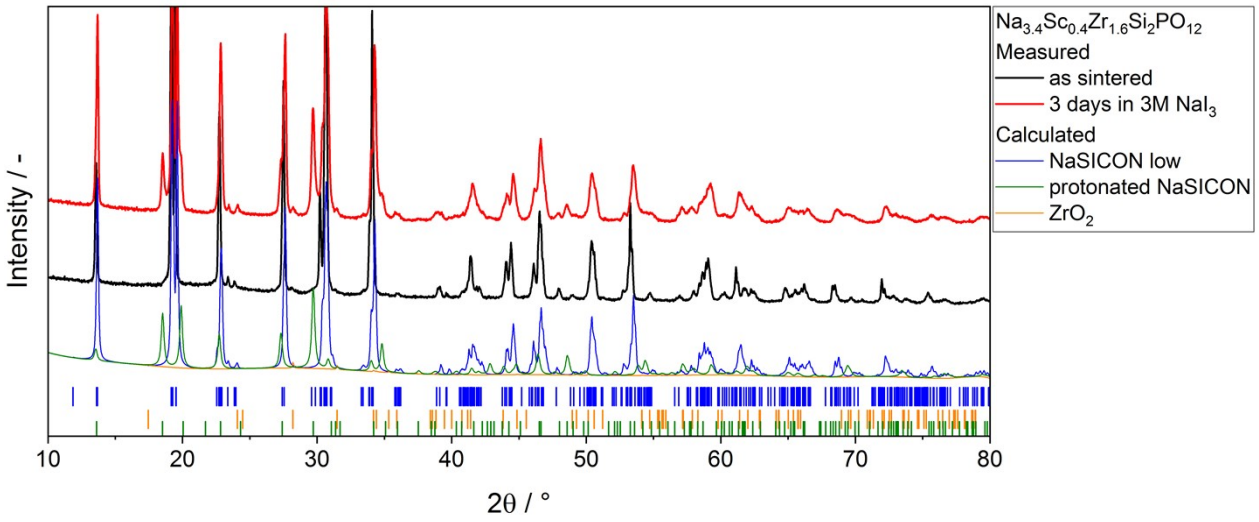


Figure S1: XRD patterns of $Na_{3.4}Sc_{0.4}Zr_{1.6}Si_2PO_{12}$ (NSZSiP3.4) as sintered (black) and after 3 days of exposure to 3M $NaI_3$ solution at 100 °C (red).

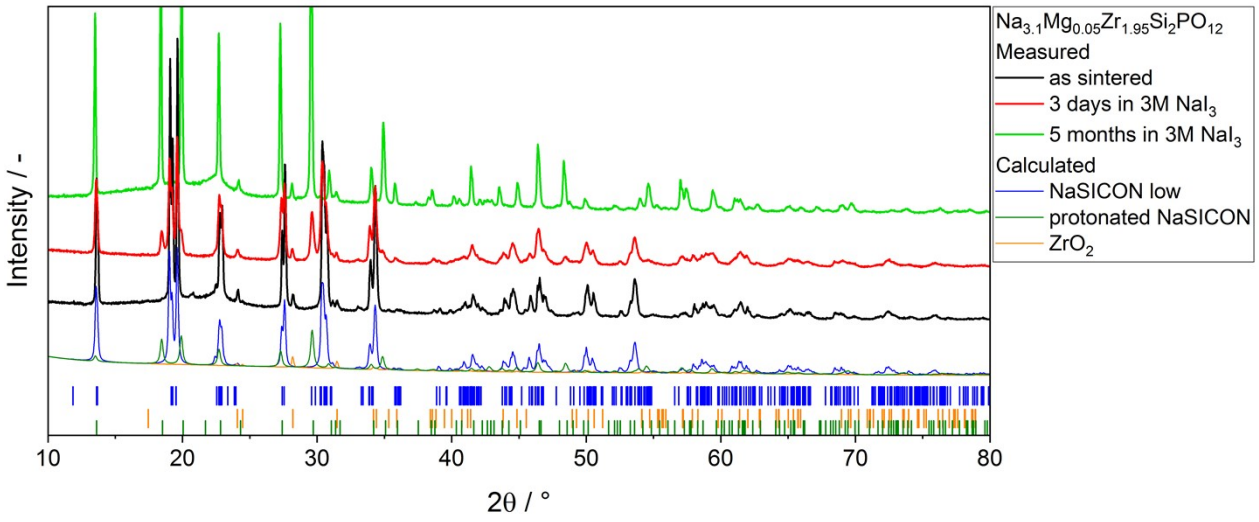


Figure S2: XRD patterns of $Na_{3.1}Mg_{0.05}Zr_{1.95}Si_2PO_{12}$ (NMZSiP3.1) as sintered (black), after 3 days (red) and after 5 months (light green) of exposure to 3M $NaI_3$ solution at 100 °C.

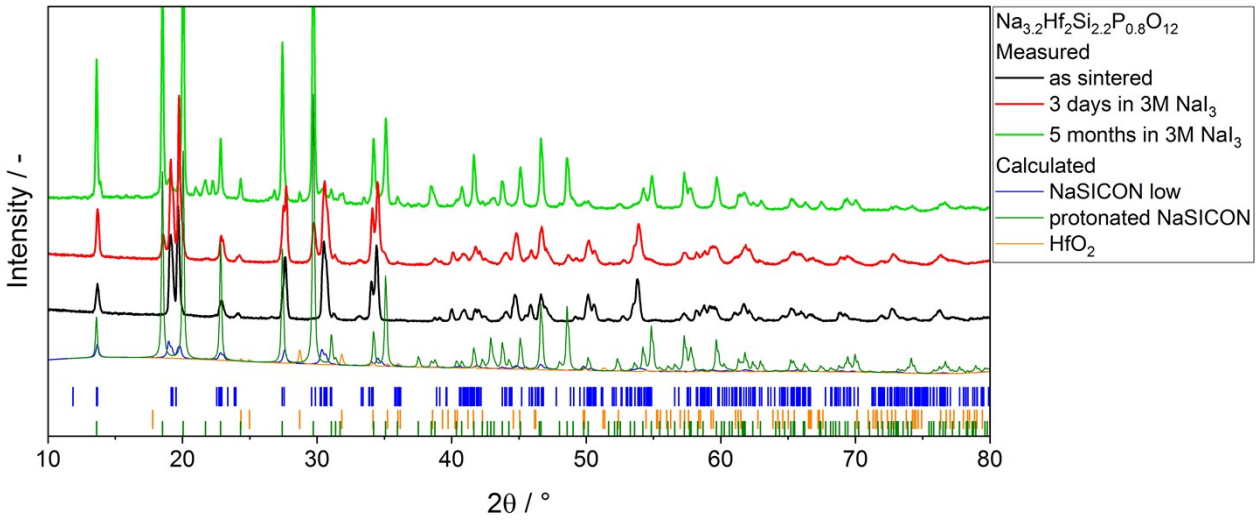


Figure S3: XRD patterns of $Na_{3.2}Hf_2Si_{2.2}P_{0.8}O_{12}$ (NHSiP3.2) as sintered (black), after 3 days (red) and after 5 months (light green) of exposure to 3M $NaI_3$ solution at 100 °C.

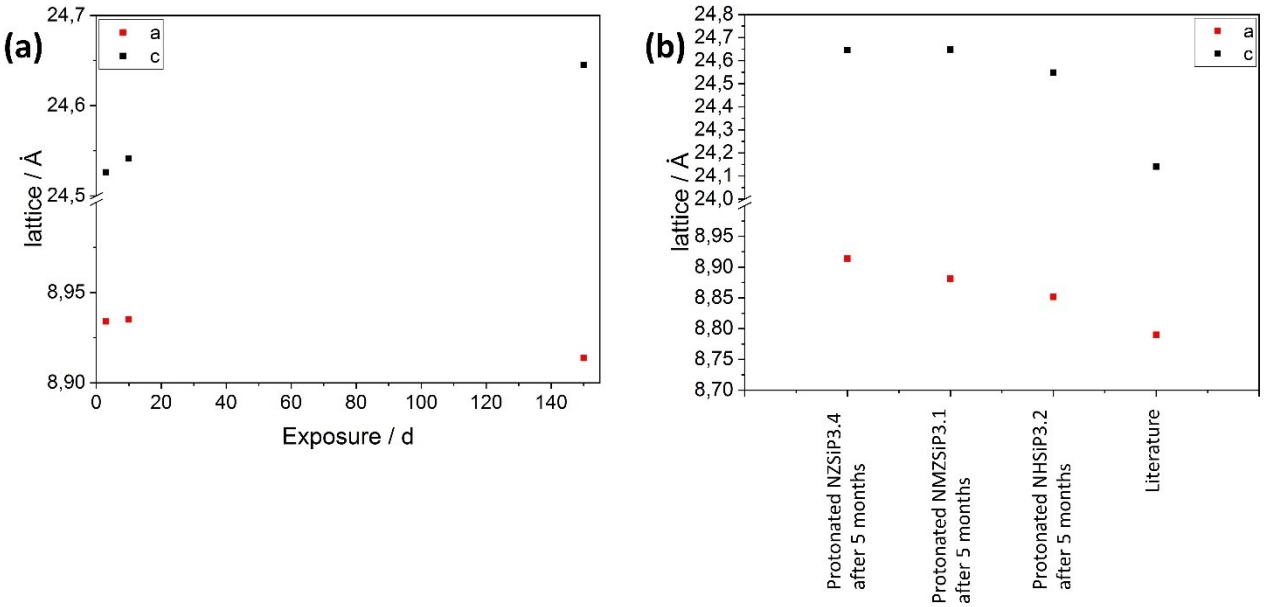


Figure S4: a) Lattice parameters of the protonated NZSiP3.4 as a function of exposure time to 3M $NaI_3$ at 100 °C. b) Lattice parameters of the protonated phase in the NZSiP3.4, NMZSiP3.1 and NHSiP3.2 in comparison to a non-protonated NaSICON material.

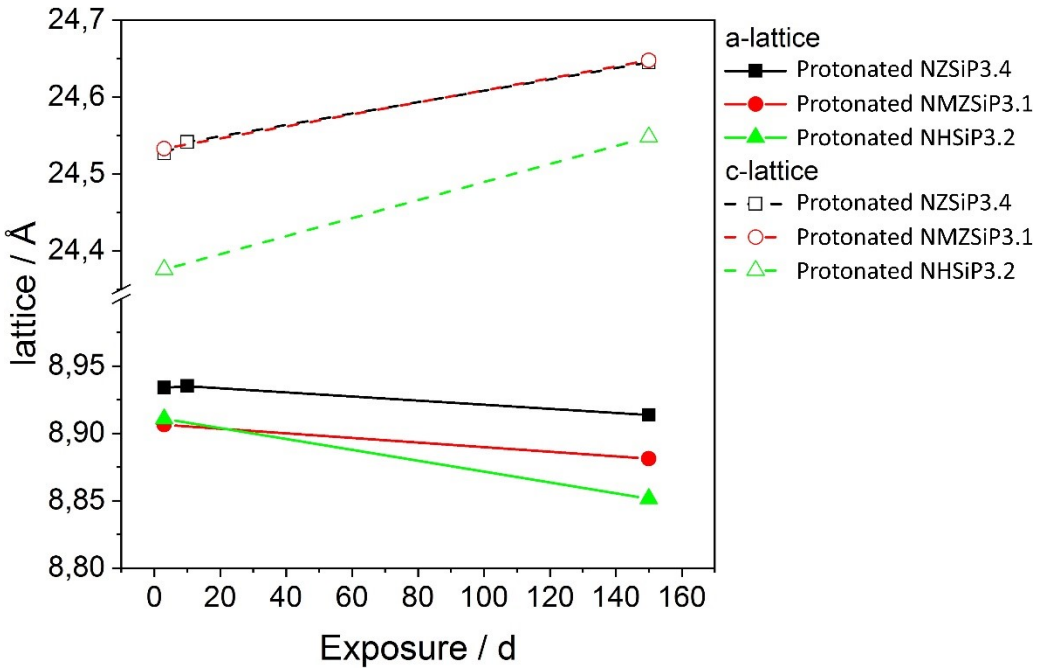


Figure S5: Lattice parameters of the protonated phase in the NZSiP3.4, NMZSiP3.1 and NHSiP3.2 as a function of exposure time to 3M $NaI_3$ at 100 °C. (Lines are guide to the eye only.)

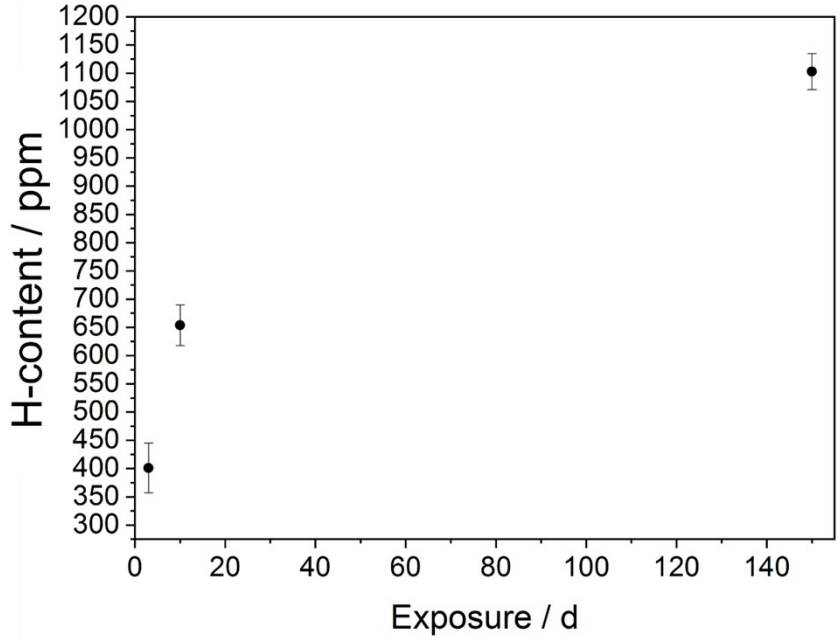


Figure S6: Hydrogen content in the NZSiP3.4 samples after exposure to 3M $NaI_3$ at 100 °C for 3 days, 10 days and 5 months.

Table S1: Summary of the phase compositions of the investigated powders as-sintered and after exposure to the respective solutions after Rietveld analysis with the ICSD data sets 38096 (NaSICON low), 202279 (basis for protonated NaSICON-Model), 81696 (NaSICON high), 18190 ($ZrO_2$) and 27313 ($HfO_2$) as reference.

| sample name | phase no. | Phase Name | space group | a (Å) | b (Å) | c (Å) | beta(°) | wt.% Rietveld |
|---|---|---|---|---|---|---|---|---|
| NZSiP3.4 as-sintered | 1 | NaSICON low | C 1 2/c 1 | 15.738 | 9.099 | 9.208 | 124.273 | 100 |
| NZSiP3.4 after 7 days in sat. NaI | 1 | NaSICON low | C 1 2/c 1 | 15.738 | 9.099 | 9.206 | 124.298 | 98 |
| | 2 | protonated NaSICON | R-3c | 8.913 | - | 24.552 | - | < 3 |
| NZSiP3.4 after 3 days in 3M NaI sol. | 1 | protonated NaSICON | R-3c | 8.928 | - | 24.515 | - | 5 |
| | 2 | NaSICON low | C 1 2/c 1 | 15.74 | 9.1 | 9.204 | 124.312 | 95 |
| NZSiP3.4 after 3 days in 3M NaI sol. at pH=1.29 | 1 | NaSICON low | C 1 2/c 1 | 15.735 | 9.099 | 9.2 | 124.297 | 90 |
| | 2 | protonated NaSICON | R-3c | 8.931 | - | 24.533 | - | 10 |
| NZSiP3.4 after 3 days in 3M NaI3 | 1 | NaSICON low | C 1 2/c 1 | 15.736 | 9.098 | 9.198 | 124.304 | 82 |
| | 2 | protonated NaSICON | R-3c | 8.934 | - | 24.526 | - | 18 |
| NZSiP3.4 after 10 days in 3M NaI3 | 1 | protonated NaSICON | R-3c | 8.935 | - | 24.542 | - | 22 |
| | 2 | NaSICON low | C 1 2/c 1 | 15.73 | 9.096 | 9.2 | 124.276 | 78 |
| NZSiP3.4 after 5 months in 3M NaI3 | 1 | protonated NaSICON | R-3c | 8.914 | - | 24.645 | - | 100 |
| NZSiP3.4 after 5 months in 3M NaI3 + 14 days in saturated NaI sol. | 1 | protonated NaSICON | R-3c | 8.913 | - | 24.645 | - | 100 |
| NScZSiP3.4 as-sintered | 1 | NaSICON low | C 1 2/c 1 | 15.716 | 9.077 | 9.185 | 124.483 | 99 |
| | 2 | Zirconium-oxide | P 1 21/c 1 | 5.144 | 5.21 | 5.311 | 99.22 | < 3 |
| NScZSiP3.4 after 3 days in 3M NaI3 | 1 | NaSICON low | C 1 2/c 1 | 15.672 | 9.06 | 9.193 | 124.205 | 74 |
| | 2 | protonated NaSICON | R-3c | 8.924 | - | 24.409 | - | 26 |
| | 3 | Zirconium-oxide | P 1 21/c 1 | 5.14422 | 5.21 | 5.311 | 99.22 | < 3 |
| NMZSiP3.1 as-sintered | 1 | NaSICON low | C 1 2/c 1 | 15.649 | 9.053 | 9.221 | 123.728 | 98 |
| | 2 | Zirconium-oxide | P 1 21/c 1 | 5.144 | 5.21 | 5.311 | 99.22 | < 3 |
| NMZSiP3.1 after 3 days in 3M NaI3 | 1 | NaSICON low | C 1 2/c 1 | 15.639 | 9.052 | 9.23 | 123.647 | 75 |
| | 2 | protonated NaSICON | R-3c | 8.906 | - | 24.533 | - | 23 |
| | 3 | Zirconium-oxide | P 1 21/c 1 | 5.144 | 5.21 | 5.311 | 99.22 | < 3 |
| NMZSiP3.1 after 5 | 1 | protonated NaSICON | R-3c | 8.881 | - | 24.648 | - | 98 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| months in 3M NaI3 | 2 | Zirconium-oxide | P 1 21/c 1 | 5.144 | 5.21 | 5.311 | 99.22 | < 3 |
| NHSiP3.2 as-sintered | 1 | NaSICON low | C 1 2/c 1 | 15.595 | 9.019 | 9.219 | 123.683 | 100 |
| NHZSiP3.2 after 3 days in 3M NaI3 | 1 | NaSICON low | C 1 2/c 1 | 15.57 | 9.01 | 9.217 | 123.57 | 75 |
| | 2 | protonated NaSICON | R-3c | 8.911 | - | 24.376 | - | 25 |
| NHZSiP3.2 after 5 months in 3M NaI3 | 1 | NaSICON low | C 1 2/c 1 | 15.466 | 9.018 | 9.262 | 123.113 | 13 |
| | 2 | protonated NaSICON | R-3c | 8.852 | | 24.548 | | 86 |
| | 3 | Hafnium-oxide | P 1 21/c 1 | 5.044 | 5.091 | 5.308 | 98.713 | < 3 |
| NZSiP3.0 as-sintered | 1 | Zirconium-oxide | P 1 21/c 1 | 5.144 | 5.21 | 5.311 | 99.22 | 3 |
| | 2 | NaSICON low | C 1 2/c 1 | 15.634 | 9.044 | 9.224 | 123.649 | 97 |
| NZSiP3.0 after 10 days in 3M NaI3 | 1 | NaSICON low | C 1 2/c 1 | 15.601 | 9.037 | 9.239 | 123.502 | 48 |
| | 2 | Zirconium-oxide | P 1 21/c 1 | 5.144 | 5.21 | 5.311 | 99.22 | 4 |
| | 3 | protonated NaSICON | R-3c | 8.903 | - | 24.527 | - | 49 |
| NZSiP3.0sub as-sintered | 1 | Zirconium-oxide | P 1 21/c 1 | 5.144 | 5.21 | 5.311 | 99.22 | 4 |
| | 2 | NaSICON low | C 1 2/c 1 | 15.679 | 9.072 | 9.231 | 123.894 | 96 |
| NZSiP3.0sub after 10 days in 3M NaI3 | 1 | Zirconium-oxide | P 1 21/c 1 | 5.144 | 5.21 | 5.311 | 99.22 | 4 |
| | 2 | NaSICON low | C 1 2/c 1 | 15.661 | 9.071 | 9.224 | 123.755 | 89 |
| | 3 | protonated NaSICON | R-3c | 8.913 | - | 24.589 | - | 8 |
| NZSiP1.0 as-sintered | 1 | NaSICON high | R-3c | 8.802 | - | 22.868 | - | 100 |
| NZSiP1.0 after 5 months in 3M NaI3 | 1 | protonated NaSICON | R-3c | 8.922 | - | 24.648 | - | 5 |
| | 2 | NaSICON high | R-3c | 8.808 | - | 22.775 | - | 95 |

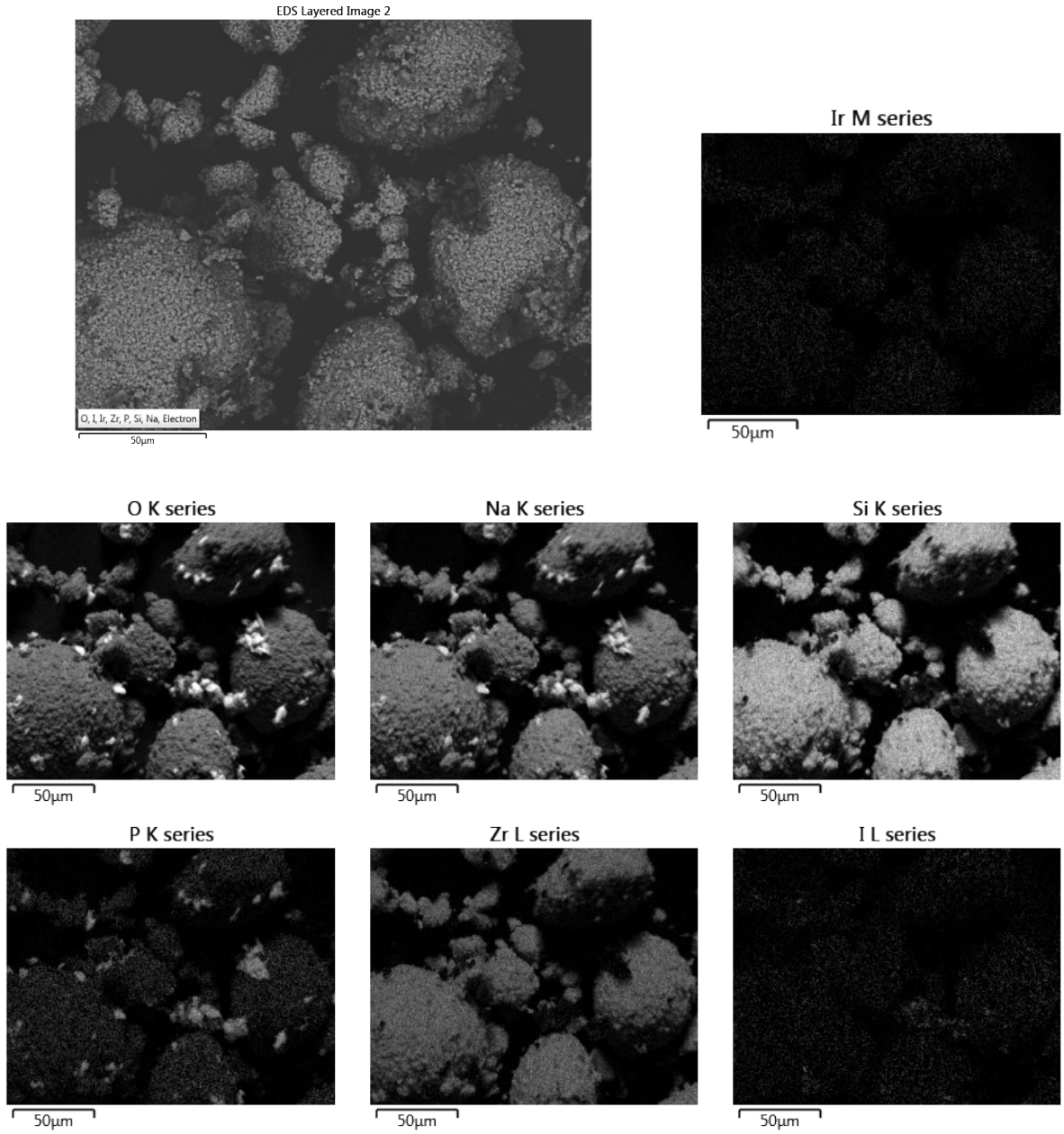


Figure S7: EDS images of sintered NaSICON powder after 3 days of exposure to 3M $NaI_3$ solution, measured on Ir-waver.

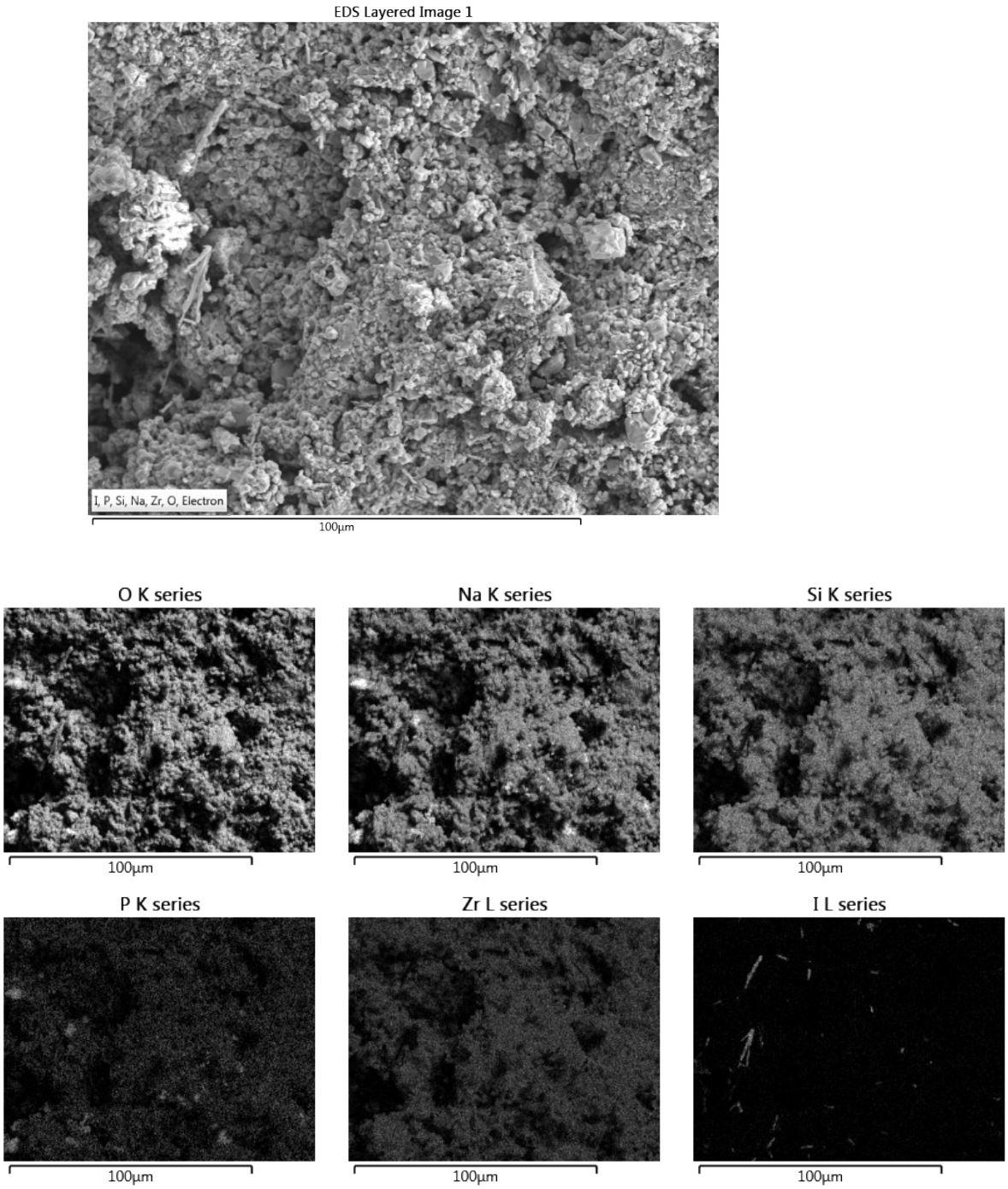


Figure S8: EDS images of sintered NaSICON powder after 10 days of exposure to 3M $NaI_3$ solution.

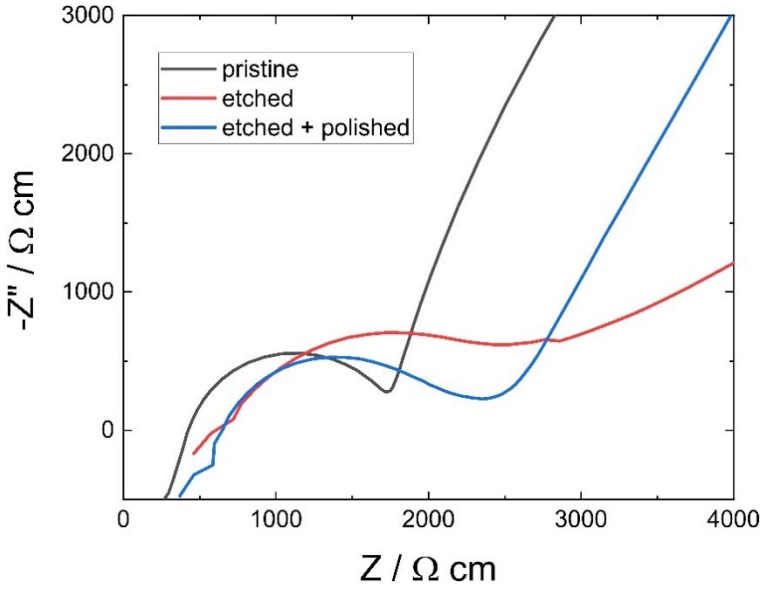


Figure S9: EIS spectra of dense $Na_{3.4}Sc_{0.4}Zr_{1.6}Si_2PO_{12}$ before and after exposure to 3M $NaI_3$ as well as after surface polishing of the etched pellet.

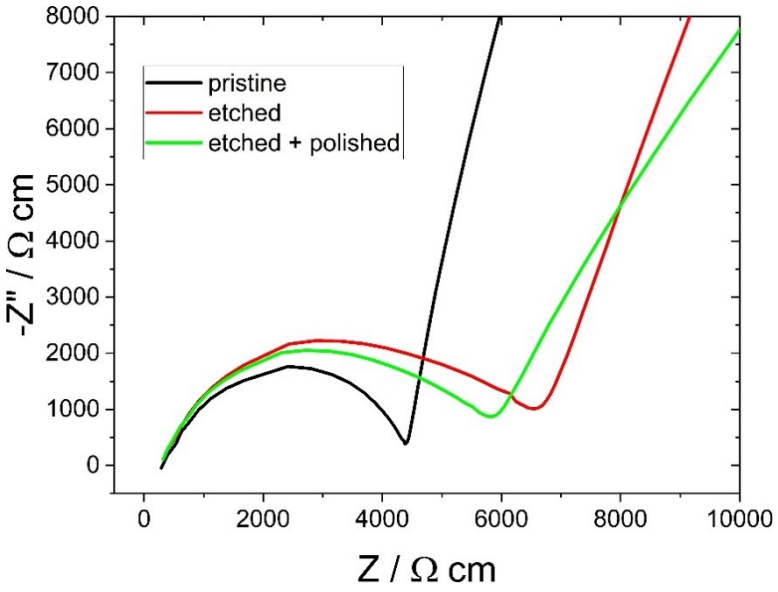


Figure S10: EIS spectra of dense $Na_{3.4}Al_{0.4}Y_{0.2}Zr_{1.6}Si_2PO_{12}$ before and after exposure to 3M $NaI_3$ as well as after surface polishing of the etched pellet.

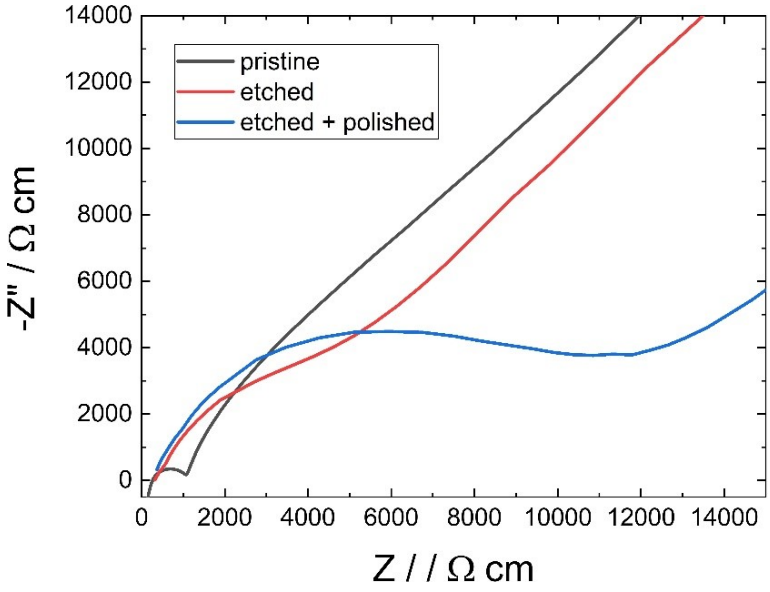


Figure S11: EIS spectra of dense $Na_{3.4}Zr_{2.4}Si_2P_{0.6}O_{12}$ before and after exposure to 3M $NaI_3$ as well as after surface polishing of the etched pellet.