Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

Poly(ionic liquid) Binders as Ion conductors and Polymer Electrolyte Interface for Enhanced Electrochemical Performance of Water Splitting Electrodes

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Experimental

Materials

1-Vinylimidazole, 1-methylimidazole, ethylbromide, 4-vinylbenzyl chloride, water-soluble nonionic azo-initiator VA86 (Wake Chemicals), and lithium bis(trifluoromethylsulfonyl)imide (TFSI; Aldrich 97%) were used as received without further purifications. All solvents used were of analytic grade.

Synthesis of *poly(1-vinyl-3-ethylimidazolium TFSI) (PIL-1)*

Monomer synthesis. 1-Vinylimidazole (4.7 g, 0.05 M), ethylbromide (6.5 g, 0.06M), and MeOH (10 mL) were added to a 100 ml two-neck round bottom glass. The mixture was stirred at 40 ^{o}C for 24 hrs, before it was precipitated into 200 ml of diethyl-ether. White solid was collected and washed with diethyl-ether several times. The powder product was dried at room temperature under high vacuum ($1\cdot10^{-3}$ mbar) till constant weight. Yield: 9.1 g (90%).

Polymerization. The monomer powder (5 g) was dissolved in water (50 mL). 2 wt% VA86 (100 mg) was then added. The mixture was degassed with argon for 30 min and then stirred at 85 °C for 24 h. After cooling down, the mixture was precipitated into ice cooled

THF (50 mL). The beige solid was filtered off and washed with THF several times. The white powder was dried at 80 °C under high vacuum for 12 h. Yield: 3.1 g (62%)

Anion metathesis. The anion exchange was then performed by adding an aqueous solution of LiTFSI into an aqueous solution of the Br containing polymer to replace Br^- by $TFSI^-$. To ensure a high degree of anion replacement, LiTFSI was added in 1.10 molar equivalent with regard to the monomer unit in the polymer.

Electrochemical measurements

All measurements were conducted either in 1 M KOH, with internal resistance (IR)-correction. A coil-shaped platinized platinum wire (PT-5W, 125 µm diameter, 99.99%, Science Products GmbH), placed along the flow channel following the electrolyte flow, was used as the counter electrode, while the reference (Hg/HgO, reference potential +0,098Vvs SHE) was inserted perpendicular to the electrolyte outlet channel. All potentials are expressed vs the RHE potential scale and IR-corrected. The potentiostat used for the electrochemical measurements is a Bio-Logic SP-150, while the embedded EC-Lab software was used to electrochemically monitor the catalysts.

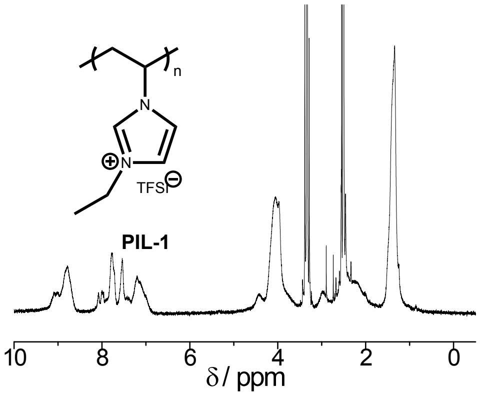
Catalyst inks were prepared by mixing by ultra-sonication 49% H_2O, 49% ethanol and 2% binder solution for 30min. Subsequently a certain amount of catalyst ink was drop casted on the glassy carbon support measuring a surface area of 0.196cm^2, previously polished with fine 0.05µm and 1.0µm alumina powder and ultrasonicated for 15min in MilliQ water, until a loading of 100µg/cm^2 was achieved. The catalyst ink was dried on the glassy carbon support under an Argon stream for 30min and finally the working electrode sample holder was inserted into the flow cell for further measurements.

The resulting electrolyte stream is continuously fed into the ICP-OES (Spectroblue EOP, Ametek) by means of a peristaltic pump at a flow rate of 0.86ml/min, through a quartz nebulizer operating at nebulizer gas flow rates of 0.85 L/min (Ar, purity 99,999%), to ensure a good balance of oxygen bubble removal from the catalyst surface and a good detection sensitivity of the catalyst corrosion products during electrochemical testing. Transient signals of Ni and Co from a $NiCoO_2$ commercial mixed oxide catalyst (Sigma Aldrich, 99% metal basis, >150nm particle size) were recorded continuously with an integration interval of 100 ms and 2 sweeps per reading. Calibration was performed using 7 standard solutions (100, 50, 10, 5, 1, 0.5 and 0 (as a blank solution) ppm metal, prepared from Merck CertiPUR®). The RF power was set to 1400 W with a plasma gas flow rate of 15 L/min. Three different binder solutions, Nafion (Nafion perfluorinated solution, Sigma Aldrich, Lot# MKBW5432V), Fumion (FAA-3m solution anion exchange ionomer solution, Lot# P1406-059) and PIL-1 were used to secure that the catalyst is attached on the glassy carbon support. As a comparison a non-binder catalyst was also prepared.

The PIL-1 binder solution was prepared similarly to the Nafion commercial solution by mixing certain amount of the PIL-1 polymer in a water and isopropanol solution until a 5 wt.% was achieved. The solution was subsequently sonicated to ensure a good mixing of the polymer in the solution.

Fourier Transformed Infrared (FT-IR) spectroscopy, (IS50 FT-IR Thermoscientific) on the PIL binder reveals its distinct vibrations at ~700 cm^{-1}, ~1200 cm^{-1} and ~1400 cm^{-1} which remail even after electrochemistry. Figures S2B and S2C show the same information as S2A but the wavenumber range is decreased to help the reader distinguish between the catalyst and PIL vibrations.

Finally Scanning Electron Microscopy (SEM) images done on a Hitachi s-5500 SEM microscope, further prove the existence of the PIL binder covering the $NiCoO_2$ catalyst. In images S3A and S3B where PIL binder was used there was a clear charging effect which is an indirect proof of a substance covering the catalyst. Additionally one can clearly see a substance covering the nanoparticles in comparison to image S3C the nanoparticles are



distinctly separated from each other.

Figure S1. ^{1}H-NMR of the PIL binder in DMSO-d_6

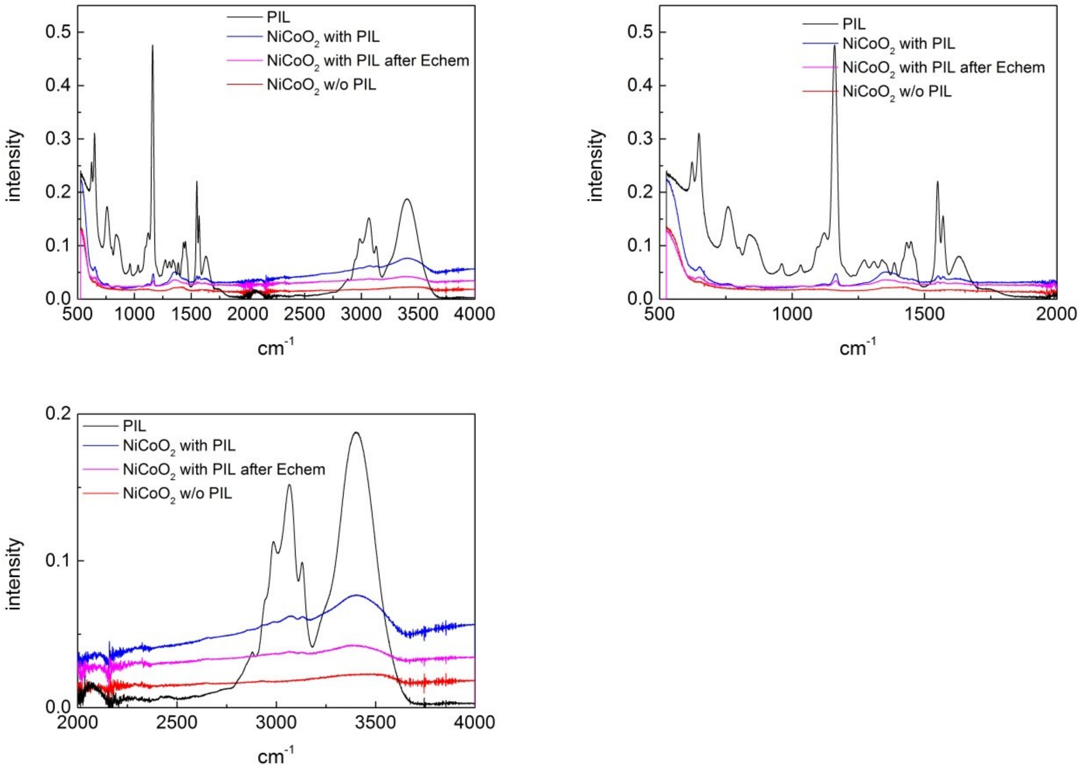


Figure S2. FT-IR measurements on PIL binder, pristine $NiCoO_2$ catalyst, $NiCoO_2$ catalyst with PIL binder before and after electrochemistry. The $NiCoO_2$ catalyst samples containing PIL, show clear signs of the PIL vibrations at ~700 cm^{-1}, ~1200 cm^{-1} and ~1400 cm^{-1}, which still remain even after electrochemistry indicating the stability of the polymer which neither dissolves nor decomposes.

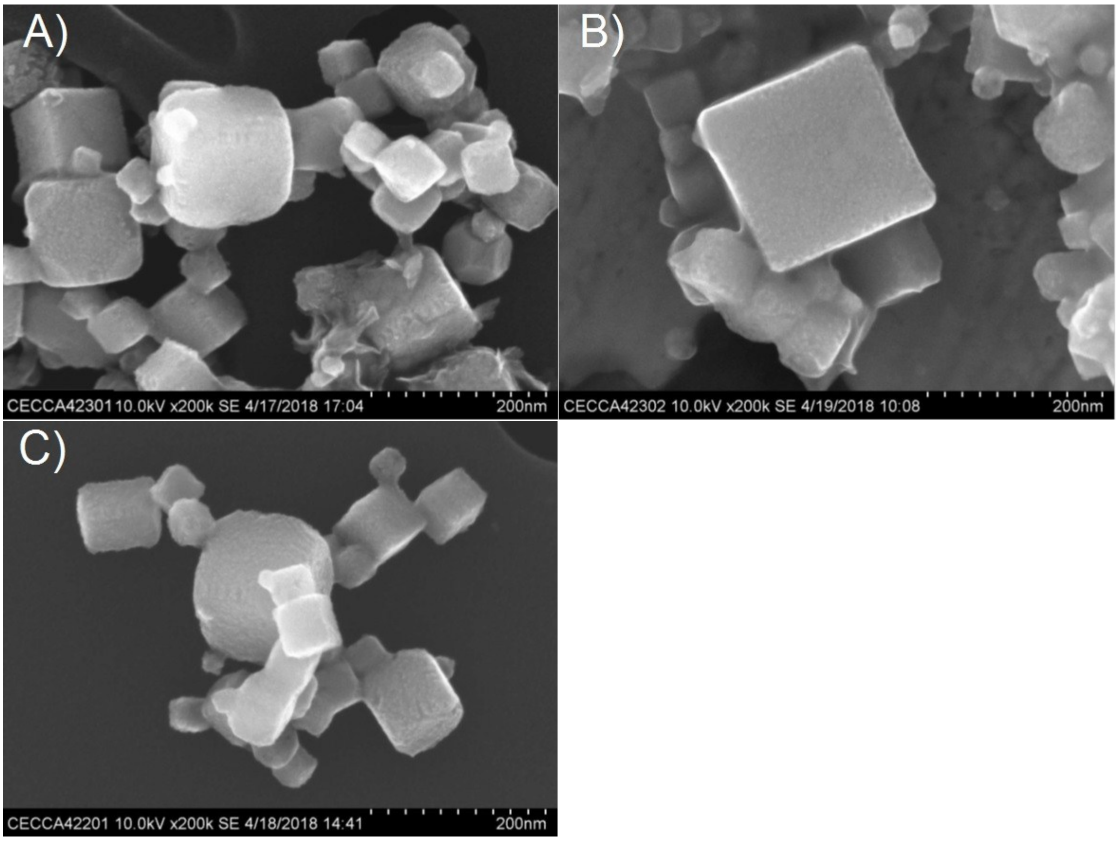


Figure S3. SEM images of a $NiCoO_2$ catalyst covered with the PIL binder A) before and B) after an electrochemical stress test at 10mA/cm^2 for 2h in 1M KOH and C) without any PIL binder.