Facile Preparation of Chloride-Conducting Membranes: First Step towards a Room-Temperature Solid-State Chloride-Ion Battery

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Supplemental Information

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Experimental Section

**Characterization and materials**

Infrared (IR) spectra were recorded on a Perkin Elmer Spectrum Two. Powder X-ray diffraction (PXRD) analyses were measured on a STOE Stadip-2 with a copper source in transmission mode. Test cells were made in standard teflon swagelock-construction and in home-made multi cells, the measurement were performed on a ARBIN battery tester with a discharge current of 0.01 mA and cut-off voltage of 0.1 V at 25°C. Cyclovoltammerty and linear sweep voltammetry measurement were performed on a Bio-Logic.. Spectra were recorded in a frequency range between $10^6$ Hz – 1 Hz by applying a small signal $V_{AC}$ with an amplitude of 10 mV.

For CV testing, a 1 cm$^2$ membrane was placed between two ITO glass electrodes (two electrode set-up) and measured at room temperature (25 °C). For impedance measurements, a piece 12 mm in diameter was punched out of the membrane material and placed between two stainless steel electrodes of a Swagelok cell and measured at room temperature (25 °C). The SEM instrument is from the company Phenix and coupled to an Oxford EDX.

Materials were purchased from Sigma-Aldrich or VWR and are technical grade. They were used without further purification.

**Membrane preparation**

**Gelatin-Chloride-Membrane:**

2.0 g of commercial gelatin powder (Oetker®) and 0.3 g tetraethylammonium chloride were added to 18 mL dimethyl sulfoxide, heated to 50 °C and stirred for 3 h. The mixture was then cooled to room temperature and continuously stirred for 2 days to ensure complete dissolution of gelatin. The solution was then heated to 50 °C and 2.8 mL glycerol was added. The solution was then poured into a petri dish and maintained at 50 °C for several days until a significant amount of solvent had evaporated. The dish was then placed in an oven at 50 °C under vacuum for 2 days to evaporate remaining solvent. The resulting product was a smooth thin layer of highly ductile gel with a slight yellow tinge.

**PVDF-Chloride-membrane:**

210 mg TBACl, 1.01 g PVDF-HF, 1 mL acetone and 1 mL PEG400 were dissolved in 4 mL DMF. The mixture was stirred and refluxed for several hours (mostly 3h). Finally, the hot mixture was cast in a petri dish. The solution is initially colorless and turns opaque after 24 h resting inside a fume hood.

**PVC-Chloride-membrane:**

130 mg tridodecylmethyl ammonium chloride and 200 mg PVC were mixed in a solution of 6 mL THF and 200 mg di-n-pentylphthalate. The mixture was stirred for
about 30 min or until complete dissolution of the starting products. The solution was cast in a petri dish and the solvent was evaporated inside a fume hood.

Electrode preparation

CuCl$_2$-cathode:
Technical grade CuCl$_2$·4H$_2$O was placed together with acetylene black and TBACl (mass ratio 70 %-20 %-10 %) in a ZrO$_2$-Ball mill. The mixture was ball-milled for a total of 4 h with 10 min milling and 10 min break at 250 rpm. The powder was used without further treatment.

PANI salt organic cathode:
The PANI salt was used directly from the commercial source without the addition of other materials.

BiCl$_3$/BiOCl·H$_2$O cathode
BiCl$_3$ was placed together with acetylene black and TBACl (mass ratio 70 %-20 %-10 %) in a ZrO$_2$-Ball mill. The mixture was ball-milled for a total of 4 h with 10 min milling and 10 min break at 250 rpm. As no further precautions are taken, parts of the starting material are easily hydrolyzed to BiOCl-hydrate; however, this does not affect battery performance as oxychlorides are often used in CIB.
S1) Problem of dissolution of anode and cathode showed in a sketch:
S2) Supplemental Analysis: IR and XRD of the membranes

PVDF-membran with references

Gelatin-membrane with reference

IR: PVC-Membrane with Reference
Gelatine-doped (0.25 g TEACl)

PVC-Membrane with reference
S3) Cole-Cole spectra of the three membranes
S4) Cavity “zinc chloride” crystal forming:

The following mechanism is proposed to explain this formation: Cavities can form at the membrane-anode interphase due to air inclusions or poor contact. During the discharge process, Zn$^{2+}$ migrates to this cavity and „ZnCl“ can form on the surface. For post-mortem analysis, the electrolyte is removed from the anode surface possibly inducing rupture and parts containing cavities remain on the surface of the anode, and thus, become visible during electron microscopy.
S5) After Discharge: elemental Bismuth is visible
S6) Conductivity of the cathode materials, normalized with thickness and size (pressed in a pellet measured at RT)
S7) PVDF-HFP and PEG400, DSC references (measured with same parameter as the membranes)