Bi_2Se_3-assisted Membrane Crystallization

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Membrane preparation

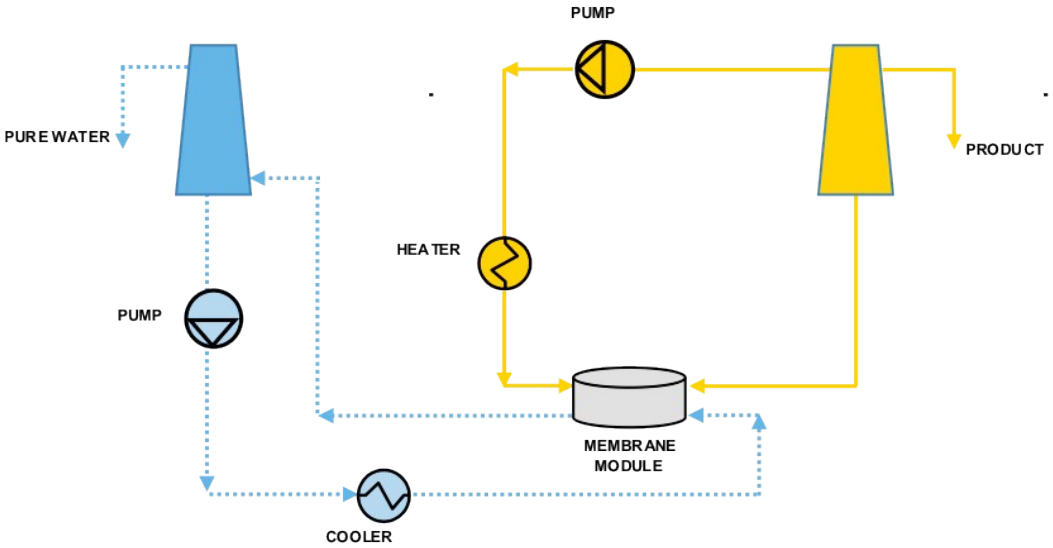
Commercial Bi_2Se_3 crystals were dispersed in NMP under vigorous mechanical stirring at 30°C for 1 h. PVDF powder (10 g) (Solef 6020, Solvay Specialty Polymers S.p.A) was added to the dispersion of Bi_2Se_3 (2 g) in NMP (71.3 g). Mixtures of PVDF (12 wt.%) and Bi_2Se_3 crystals (20 wt% with respect to polymer) were obtained after 24 h of mechanical stirring at 30 °C. After degasing, the solution was cast on glass plate by using a casting knife regulated on 300 μm (Elcometer Instruments Inc.) and coagulated for 5 min in a bath containing IPA in order to promote solid–liquid demixing. Solutions based on pristine PVDF and related membranes were prepared according the same procedures.
After washing in deionized water, each set of membranes was air-dried at room temperature and, then, annealed at 30 °C for 1 h.

Membrane characterization

The scanning electron microscopy (SEM; Quanta 200, FEI Company) was used to analyze the morphology of the hybrid membrane in SEM and BSE mode. Raman spectroscopy measurements were carried out on the hybrid- membranes at room temperature using a Renishaw inVia confocal Raman microscope, with a solid state green laser (λ = 532 nm) and a 50x objective. XRD pattern were detected by using PANalytical Empyrean X-ray diffractometer equipped with a 1.8 kW CuKα ceramic X-ray tube, PIXcel3D 2x2 area detector and operating at 45 kV and 40 mA. The diffraction patterns were collected in air at room temperature using Parallel-Beam (PB) geometry and symmetric reflection mode.
Infrared analysis in ATR mode was performed collecting the spectra at a resolution of 4 cm^{-1} by using a Spectrum One System Diamond (PerkinElmer Instruments). The overall porosity was expressed as a ratio of void spaces in membrane over the total volume of the membrane. The void space was estimated by wetting the samples with a fluid at low surface free tension (kerosene).
XPS measurements were performed in normal incidence at the BACH beamline of the Elettra synchrotron, Trieste (Italy) by means of a Scienta R3000 hemispherical analyser. Oxygen and water were dosed by means of leak valves. Spectra for 1s-O core levels for Bi_2Se_3(0001) have been recorded after exposition at room temperature to a dose of 2000 Langmuir (10^{-6} torr·s) of O_2 and to 1000 Langmuir of H_2O The photon energy was 654 eV.
Breathability tests were carried out following the upright cup gravimetric procedure (ASTM E96B). The membrane-sealing flasks filled with ultrapure water were equilibrated for 1 h at different temperatures (T = 25 to 65 °C) and, then, placed in a box containing a silica gel as a desiccant. The loss of water vapor was estimated after 24 h and expressed as a ratio of the weight variation of the water and the membrane area per day [($gm^{-2}day^{-1}$)]. The measurements were repeated on three sample specimens with an error less than 10 %.

Membrane Distillation and Crystallization tests

Thermally-driven MD and MCr experiments were executed accordingly with the Membrane Direct Contact (DC) configuration using NaCl solutions 0.6M, the typical salt concentration in seawater, and 4M, which is a supersaturated solution (Scheme 1). Two different feed flow rates = 20 and 60 mL/min and sets of temperature feed = 38 and 50 °C and $T_{perm.}$ = 16.5 and 19.5 °C were applied for MD experiments, whereas membrane crystallization was carried at T_{feed} = 21.96 °C and feed flow rate of 100 mL/min.
Retentate and distillate streams were converged, in a counter-current way, toward the membrane module containing the membrane, where the liquid water was evaporated. On the retentate side (continuous orange line), a pump was taking and sending the heated feed to the membrane module. Also on the distillate side (dotted blue line), a second pump ensured the counter-current recycle of the cold stream in order to remove from the solution the vapor diffusing through the membrane pores. The trans-membrane fluxes were estimated by evaluating the weight variations in the distillate tanks. The salt conductibility of the feed and permeate streams were measured by using a conductive meter (Eutech Instruments PC 2700). Because the goal in membrane crystallization was to concentrate and crystallize the salt (NaCl) contained in the feed, water vapor was continuously removed from the feed solution in order to reach supersaturation. Sodium chloride crystals produced were observed by using an optic microscope (ZEISS, model Axiovert 25) and pictures recorded with a video-camera module VISIOSCOPE Modular System equipped with optical head (10/100X). Crystals were characterized according to different parameters, including crystals shape, dimension and growth rate. The evolution of particle size distribution as function of time allowed one to evaluate quality, coefficient of variation (*CV*), mean diameter (dm) and growth rate of the produced crystals (*G*).



Scheme 1. Schematic representation of a membrane distillation/membrane crystallizer plant.