

Experimental

Materials: 4,4'-(Hexafluoroisopropylidene) dipthalic anhydride (6FDA), 2,3,5,6-tetramethyl-p-phenylenediamine (Durene diamine), acetic anhydride ($\geq 99\%$), acetylacetone ($\geq 99.3\%$), trimethylamine (TEA, $\geq 99.5\%$), Molecular sieve 13X (2 μm average particle size), sodium nitrate (NaNO_3) and copper (II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) were purchased from Sigma-Aldrich Co. The 6FDA dianhydride and Durene diamine monomers were purified via recrystallization in acetic anhydride and methanol respectively.

N,N-dimethylacetamide (DMAc), chloroform, methanol and ethanol were HPLC grade and purchased from Daejung Chemicals and Metals Co. (South Korea). All the solvents were purified via vacuum distillation.

Synthesis of encapsulated zeolite: The zeolite encapsulation was performed in three-step procedure. At the first step, ion exchange of X-type zeolite was performed by treating the zeolite with solution of copper (II) sulfate in distilled water (1 M) in a ratio of 1:10 (w/v). After letting the mixture stir for 24 h at 90 °C, the resulting suspended product was filtered and washed with hot distilled water until the filtrate became colorless. The light blue Cu(II) exchanged zeolite was filtered and washed with distilled water and subsequently dried in an oven at 100°C for 24 h.

At the second step, a suspension 10% (w/v) of Cu(II) exchanged zeolite in methanol was prepared and 100 mM of Durene diamine was added to the mixture and stirred at 90 °C for 24 h until the suspension color turned to dark blue and the diamine-copper complex was formed and entrapped into the zeolite cages. The suspended particles were filtered and washed by hot ethanol and after drying in an oven at 100°C, the product was washed with a solution of sodium chloride (100 mM in distilled water) with stirring for 24 h at 90 °C in order to re-ion exchange any unreacted metal ion from the product. The suspended particles were filtered and washed by Soxhlet extraction with ethanol for 24 h to remove the adsorbed complex stuck to the zeolite surface. The obtained product dried in an oven at 100°C for 24 h until the product weight became constant.

At the last step, the polyaza macrocyclic copper complex was completed at zeolite cages via a template condensation reaction between the diamine-copper complex and diketone; 10% (w/v) suspension of diamine-copper complex/ NaX (resulting from previous step) in methanol was prepared and 100 mM of acetylacetone was added drop by drop to the suspension and stirred at 90°C for 24 h until the suspension color turned to dark blue. The suspended particles were filtered and washed with hot ethanol several times and dried in 100°C oven for 24 h. The obtained powder was washed by Soxhlet extraction with ethanol for 24 h and the resulting product was dried in 100°C oven for 24 h and the product denoted as $[\text{Cu}(6\text{L})]^{2+}@13\text{X}$.

Synthesis of 6FDA-Durene polyimide: The 6FDA-Durene polyimide was synthesized by a two-step poly condensation reaction via a poly(amic-acid) precursor, because of the high efficiency of two-step polymerization method for aromatic polyimides preparation ¹. In the first step, poly(amic-acid) was synthesized by the addition of 6FDA to a moisture-free solution of Durene in DMAc. The total solid concentration (including equimolar of diamine and dianhydride) was 20 wt.%. The solution was stirred in an ice bath for 24 h under nitrogen atmosphere to achieve a viscous poly(amic-acid) solution. In the second step, acetic anhydride as the dehydrating agent and trimethylamine (TEA) as the basic catalyst were added into poly(amic-acid) solution (with the mole ratio of 4:1) and reacted for 24 h at room temperature. In this step, the poly(amic-acid) was dehydrated to polyimide via the chemical imidization. Subsequently, the 6FDA-Durene polyimide was precipitated in methanol, the polymer was collected by filtration and washed with methanol several times and dried at 100 °C in air circulating oven for 24 hours. The polymerization yield was 93%.

Fabrication of membranes: The membranes were fabricated via solution casting/solvent evaporation method. 6FDA-Durene polymer was dissolved in chloroform with 5 wt.% and stirred for 24 h at ambient temperature. After the polymer was completely dissolved, the solution was degassed and casted in a Petri dish to prepare neat polymeric membrane. The MMMs were fabricated with different loading of [Cu(6L)]²⁺@13X in the range of 0-20% (based on the polymer weight) using the priming method. The desirable amount of [Cu(6L)]²⁺/13X was suspended in chloroform solvent and stirred for 6 h at room temperature. The suspension solution was primed by adding 10 % of the total amounts of 6FDA-Durene polymer and stirring for 12 h at room temperature. The remaining polymer (90%) was then mixed with the primed solution, followed by stirring another 12 h. The ([Cu(6L)]²⁺@13X)/polymer concentration in chloroform was 5 wt.% in all samples. The prepared solution was casted in Petri dish after degassing and the casted membranes were dried at room temperature and subsequently placed in 100°C vacuum oven for 24 h to evaporate the residual solvent.

Characterization: 1) zeolite particles: Elemental analysis of the zeolite particles was performed via X-ray fluorescence (XRF) spectroscopy (PW 2404 Philips Holland) and CHN analysis (LECO TruSpec CHN analyzer). The ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) spectra of the samples was acquired with an Avantes AvaSpec-2048-TEC spectrometer in the wavelength range of 190 to 750 nm. Wide-angle X-ray diffraction was measured on a Panalytical Empyrean diffractometer using CrK α radiation at a wavelength of 2.289 Å, accelerating voltage of 40 kV, in a 2 θ range of 5–100° at 25°C. The size distribution of particles was determined using DLS spectrophotometer (QuDix, Scatteroscope, Korea). The morphology of the zeolite particles was observed by field emission scanning electron microscope (FESEM, MIRA3 TESCAN) at acceleration voltage of 15.0 kV. The Branauer, Emmett and Teller (BET) method was employed to measure the specific surface and pore size distribution

of zeolite particles using Belsorp-mini volumetric adsorption apparatus. Equilibrium CO₂ adsorption experiments was conducted at 308 K in the pressure range of 1–10 bar via the volumetric method in a batch set up which has been described by details elsewhere ². **2) 6FDA-Durene polymer:** ¹HNMR spectrum of synthesized 6FDA-Durene was obtained with a Bruker Avance (300 MHz) spectrometer using CDCl₃ as solvent. The gel permeation chromatography (GPC) system (Shimadzu LC-20A, column model: HR4, mobile phase: THF, polystyrene standard) was applied to measure the molecular weight of synthesized 6FDA-Durene. **3) Membranes:** Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were recorded by Perkin-Elmer spectrophotometer in the spectral range of 600–3800 cm⁻¹ at resolution of 4 cm⁻¹. Wide-angle X-ray diffraction was measured on a Panalytical Empyrean diffractometer using CrK α radiation at a wavelength of 2.289 Å, accelerating voltage of 40 kV, in a 2 θ range of 5–100° at 25 °C. The cross-sectional morphology of the freeze-fractured membranes were observed by field emission scanning electron microscope (FESEM, MIRA3 TESCAN) after sputter coating with gold at acceleration voltage of 15.0 kV and magnification of 2.00 kx. Mechanical strength of the prepared membranes was investigated using SANTAM tensile testing Machine at room temperature.

Gas permeation measurements: The gas permeation of prepared membranes was measured by a variable-pressure/constant-volume apparatus which has been described by details elsewhere ³. The permeation experiments for CO₂, CH₄ and N₂ was carried out at feed pressure ranging from 2 to 10 bar and at temperature of 35°C. Experiments were repeated for three same sample of each membrane, to ensure the validity of the experimental results.

The permeability of the membranes was calculated with Eq.1:

$$P = \frac{273.15 \times 10^{10} VI \left(\frac{dp}{dt} \right)}{AT(P_0 \times 76)} \quad (1)$$

The ideal selectivity of one penetrant over another was calculated through Eq. 2:

$$\alpha_{i/j} = \frac{P_i}{P_j} \quad (2)$$

where $\alpha_{i/j}$ is the ideal selectivity, P_i and P_j represent the permeability of pure gas i and j respectively, in the same conditions.

1. C. E. Sroog, *Prog. Polym. Sci.*, 1991, **16**, 561-694.
2. M. Rasoolzadeh, S. Fatemi, M. Gholamhosseini and M. A. Moosaviyan, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, 2008, **27**, 127-134.
3. H. Sanaeepur, S. Mashhadikhan, G. Mardassi, A. Ebadi Amooghin, B. Van der Bruggen and A. Moghadassi, *Korean Journal of Chemical Engineering*, 2019, **36**, 1339-1349.