Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Bio-mimetic Oxygen Separation via Hollow Fiber Membrane Contactor with O_2 Carrier Solutions

Mahdi Fathizadeh,[a] Konstantin Khivantsev,[a] Travis J. Pyrzynski,[b] Naomi B. Klinghoffer,[b] Abolfazl (Nabi) Shakouri,[a] Miao Yu,[*a] and Shiguang Li[*b]

[a] Department of Chemical Engineering, University of South Carolina, Columbia, SC 29208, USA

[b] Gas Technology Institute, 1700 S. Mount Prospect Road, Des Plaines, IL 60018, USA

[*] Corresponding author: shiguang.li@gastechnology.org

Co-corresponding author: yum5@rpi.edu

EXPERIMENTAL METHODS

Regents. Branched poly(ethyleneimine) (PEI) (average M_n ~60,000 by GPC, average M_w ~750,000 by LS, 50 wt. % in H_2O), and Cobalt chloride ($CoCl_2$) were purchased from Sigma-Aldrich. Ultra-pure air and oxygen (>99.993) were supplied from Airgas company. Ultrapure deionized water generated by RO/DI water purification unit by Mar Cor Purification was used for all experiments.

Preparation and characterization of O_2 carrier solution

We prepared 1mol/L (based on CH_3CH_2N unit) aqueous solution of PEI and 1mol/L aqueous solution of $CoCl_2$, and then mixed them at different volume ratios to prepare PEI-Co complexes with different molar ratios of amine functional groups to Co. For example, 10 ml of PEI solution is mixed with 1 ml $CoCl_2$ solution to obtain a ratio of 10. We fixed the volume of cobalt chloride solution at 1 ml for all the O_2 carrier solution preparation.

The prepared PEI-Co complex solution as characterized by ATR-IR, electron paramagnetic resonance (EPR), Raman, stopped-flow UV-VIS, and viscosity.

ATR-IR: To further confirm the absorption of oxygen by PEI/Co solution with time, Attenuated total internal reflectance-Fourier transform infrared, ATR-FTIR spectra of PEI/Co oxygen complex, were collected using a Nicolet Nexus 470 FT-IR spectrophotometer (Thermo Fisher Scientific, USA) over the range of 4000-600 cm^{-1} at a 4 cm^{-1} resolution. The PEI and Cobalt solutions were mixed in the absence of oxygen, and a film of Co-PEI was then quickly deposited on a ZnSe crystal. ATR spectra were immediately collected upon exposure to oxygen, with the initial unoxidized Co-PEI film serving as a background, thus allowing us to obtain difference spectra in time.

Viscosity: Viscosity of PEI/Co solution was measured at ambient temperature using a glass capillary viscometer (50 L199, Cannon Instrument Company). The glass capillary viscometers were filled with the GO dispersion by using suction to pull solution to the upper mark of calibrated volume inside of the viscometer. Flowing time of the liquid down to the lower calibrated mark of the glass viscometer was measured. The provided calibration constant by the manufacture was used to calculate the viscosity of PEI/Co solutions. The viscosity of PEI/Co with oxygen complex as a function of PEI/Co ratio was shown in Table 2.

EPR: Co(II)-PEI solutions with DI de-aerated water were mixed in a Siemens oxygen-free glove box, loaded in the EPR quartz cells under oxygen free environment and sealed with a septum. EPR spectra were recorded using a Bruker EMXplus spectrometer equipped with an Oxford Instruments ESR900 liquid helium continuous flow cryostat under the following conditions: temperature 5 K, modulation amplitude 10 G, microwave power 2 mW. A total of 5 scans were collected for each sample. For oxygenated species, UHP oxygen was bubbled through the Co-

PEI solution directly in the EPR tube for a ~15-30 seconds, the solution was immediately frozen with LN afterwards and EPR measurements were performed at 5 K.

Raman: Raman measurements were conducted using a Jasco NRS-3100. The spectrometer was coupled to an Olympus microscope; sample observation and analysis were performed using Olympus objective 100x equipped with a cooled charge-coupled device (CCD) detector. CCD integration time was varied between 1 to 30 seconds. In case of samples creating weak signals, the time was increased to attain a good signal to noise ratio of spectrum. The power was typically ~100 mW at the sample. A calibration curve for Raman shift is needed which can be done by comparing the Raman spectrum of silicone file obtained by the experiment and the true and accurate peak values from literature.

Stopped-flow UV-VIS: Stopped-flow UV-VIS measurements were performed on an Applied Photophysics Ltd. SX20 stopped-flow spectrophotometer. Single wavelength traces were taken using a photomultiplier tube and full spectrum data were collected by photodiode array. Co(II) ([Co(II)]=1*10^{-5} M in the final solution) and PEI solutions (PEI(N):Co=20 in the final solution) were saturated with oxygen prior to measurements ([O_2]=4*10^{-4} M) and mixed immediately in the stopped flow apparatus.

O_2 absorption measurements

Batch system:

Oxygen absorption of the PEI/Co solution was studied using a batch system shown in Figure 1S. In a typical measurement, a fresh PEI/Co complex solution, prepared by mixing poly(ethyleneimine) (PEI) and $CoCl_2$, was added to a liquid container, which was then sealed by a cap equipped with a pressure sensor to monitor the gas phase pressure. Oxygen partial pressure and PEI/Co ratio on absorption kinetics were investigated.
The absorbed amount of oxygen can be calculated by the following equations:

$$n_t = \frac{P_t V}{RT} \quad (1)$$

$$\Delta n_t = n_0 - n_t \quad (2)$$

Where n_t: total mole of gas phase; P_t: gas phase pressure at time t; V: gas phase volume of the container; R: ideal gas constant; T: temperature; n_0: initial mole of the gas phase; n_t: mole of the gas phase at time t; and, Δn_t: amount of oxygen absorbed.

Membrane contactor system:

The concentration of nitrogen and oxygen at retentate gas was measured using the below system (figure S2). Hollow fiber module was contacted to air tank which equipped with mass flow meter (MFC). The mass flow meter was used to control the feed flow rate at 5, 10, and 15 SCCM. In the shell side, the peristaltic pump was used for recycling PEI/Co solution during absorption. PEI/Co solution with ratio 10 was filled at shell side and gas flowed into the hollow fibers. The retentate gas connected to the oxygen analyzer.

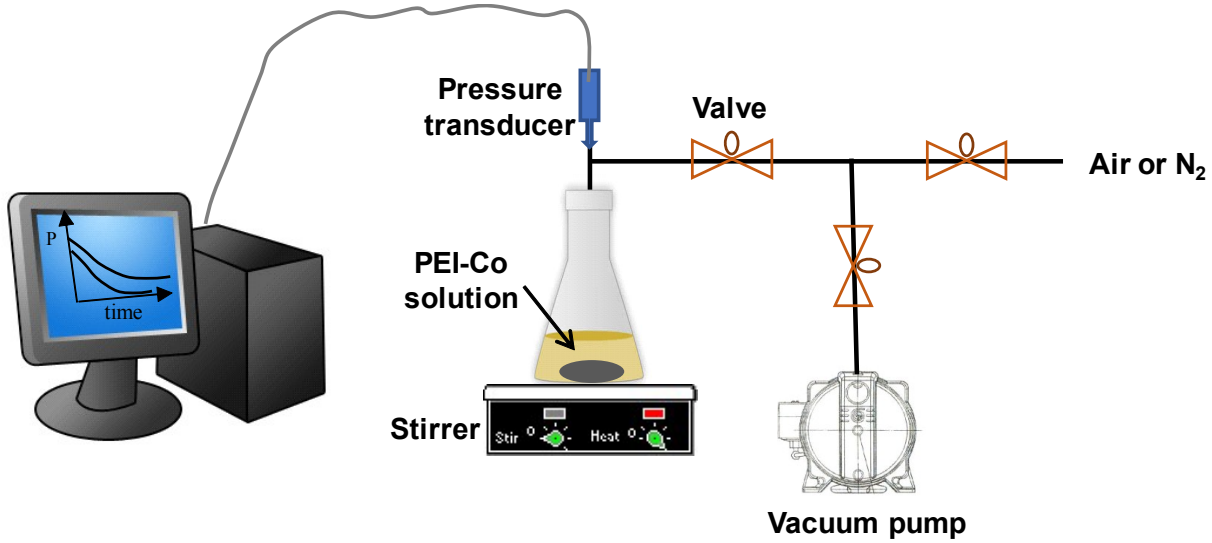

Figure S1. Schematic of the system for O_2 absorption capacity and kinetics measurements at room temperature.

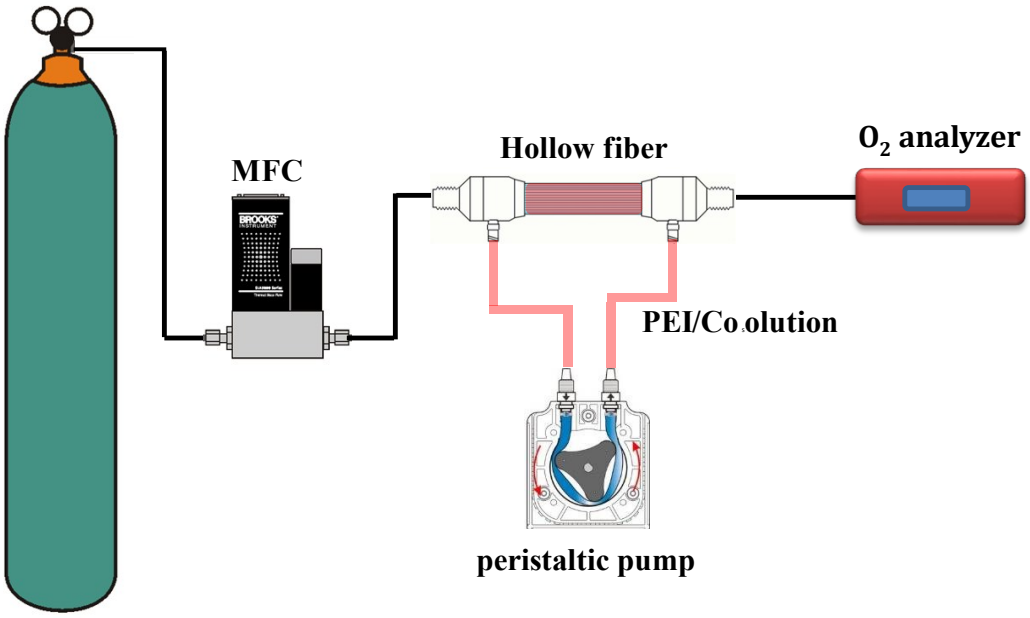

Figure S2. Schematic of a flow system for O_2 absorption from air in a membrane contactor.

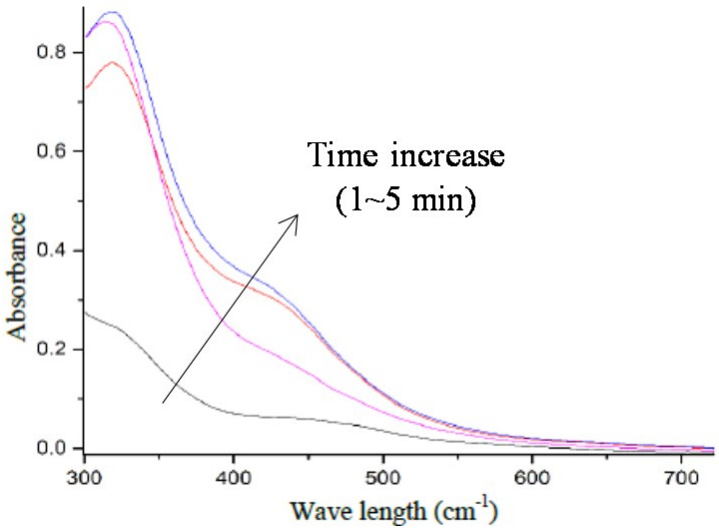

Figure S3. Representative spectra for the kinetically distinguishable cobalt containing species during stopped flow UV-VIS spectra.