A Survey of the Development of Membrane Science and Technology in China

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1. History of membrane development

The research and development on membrane science and technology in China were started from ion exchange membranes in 1958.

Exploring research on reverse osmosis (RO) membranes was set about in 1965.A national joint research project on sea water desalination began in 1967.This played an important role in training research team and laid a good foundation for the progress of membrane science and technology.

It entered the developing stage in 1970s, a magnificent period for membrane research and development. The membranes and related modules on electrodialysis (ED), RO, ultrafiltration (UF) and microfiltration (MF) had mostly been developed in this period. At the same time, a study on liquid membrane (LM) was also started.

It stepped into application and popularization stage in 1980s,and also a developing period for new membrane processes. A great success was achieved in this period. Seawater and brackish water desalination, pure and ultrapure water production, separation, purification and concentration of various liquids by membrane technology were put into application, some of them in large scale. At the same time, gas separation (GS) membranes developed very quickly. The membrane processes for oxygen enrichment and separation of N_2/H_2 entered pilot period. Study on synthesis of perfluorosulfonic and carboxylic ion exchange membrane was also got good results. Studies on pervaporation (PV), membrane distillation (MD), membrane extraction (MEx), membrane phase separation, inorganic membranes (IM) and membrane reactors (MR) were also initiated.

In 1990s,composite membranes for RO and NF were manufactured in pilot scale. GS for N_2/H_2 were widely used in fertilizer factories. Preparation and preliminary application of inorganic membranes and new type of ion exchange membranes, sea water desalination by reverse osmosis and dehydration by pervaporation etc were also realized. Sea water desalination, water reuse by membrane processes and membrane application in bioengineering have been also launched.

2. Brief introduction for each of the membrane processes

2.1 Ion Exchange Membranes and ED

The research on ion exchange membranes began in 1958 with the first membrane based on PVA. Since then many types of membranes have been studied and developed, but the most widely used are heterogeneous membranes of polystyrene-divinylbenzene. The annual production of the membranes has reached more than 400,000 square meters in recent years.

Table 1. Properties of heterogeneous and new homogeneous ion exchange membrane

Type		Thickness (mm)	Water content (%)	IEC meq./g	Resistance (Ω-cm^2)	Permselectivity	Blast strength (Mpa)
Heterogeneous*	3361 (cation-exchange)	0.4-0.5	35-50	≥2.0	≤12	≥92	>0.3
	3362 (anion-exchange)	0.4-0.5	35-45	≥1.8	≤13	≥90	>0.1
Homogeneous**	DD-120-A (anion-exchange)	0.25	49	1.96	2.0	98	>0.8
	DF-120-C (cation-exchange)	0.22	44	1.57	1.4	92	>0.7
	DF120-A (anion-exchange)	0.25	49	1.96	2.0	98	>0.8

*material is polystyrene-divinylbenzene **material is cross-linked PPO

The applied theories studied on ED including concentration polarization, water splitting, Electrode behavior and hydrodynamics in compartments were mainly conducted in 1970s.

There are many configurations of ED/EDR units with the largest size of the membrane/spacer area of 1600×800mm.More than 1000 ED units have been produced each year from nearly 40 factories.

The ED process has been widely used in brackish water desalination, pure and ultrapure water production, waste water treatment and by-product recovery.

In addition, studies on bipolar membranes and CDI (EDI) processes have been also carried out. CDI prototypes and equipments with unit capacity of 1-3m^3/h were operated for pure water production.

2.2 RO, UF, MF and Nanofiltration (NF)

The study on RO was started in 1965.The research on UF and MF is from the beginning and in the middle of 1970s respectively.

Flat and tubular cellulose acetate (CA) asymmetric RO membranes, including CA, CA-CTA & CAB, studied first in 1960s. Studies on aromatic polyamide membrane materials, including PSA, and related hollow fiber RO membranes, and CTA hollow fiber RO membranes were started at the beginning of 1970s. Studies on RO composite membranes formed by interfacial polycondensation and in-site polymerization, and dynamically formed membranes as well as SPS membrane began in the middle of 1970s. Table 2 shows performance of polysulfone amide (PSA) RO membranes developed in 1970s-1980s. Table 3 shows performance of composite positively-charged membranes developed in 1980s for UF of cathode electrophoresis paints.

Table 2. Performance of polysulfone amide (PSA) RO membranes

Type	Performance		Test condition			
	Flux(1/m^2.h)	Rejection(%)	Operating pressure (MPa)	Feed concentration (mg/l)	Temperature (℃)	pH
PSA-1	43	98.2	5.0	300(NaCl)	25	7.0
PSA-2	17.6	99.3	4.0	2700(Cd^{2+})	25	12.0

Table 3. Performance of composite positively-charged UF membranes

Type	Performance		Test condition		
	Flux(1/m^2.h)	Rejection(%)	Operating pressure (kPa)	Paint concentration (%)	Temperature (℃)
HN-01	25	99	150	20	25

The membrane has excellent properties of resistance to oxidation of low concentration of Cr^{6+} at pH 2-12, and been used for the treatment of electroplating rinse water.

Spiral wound and hollow fiber modules have been widely used in RO and UF processes.

The pleated filter cartridges and flat sheets are the main usable forms in MF.

There are more than 100 factories manufacturing varieties of RO, UF and MF membranes, modules and plants. Most of them have been also serving related engineering.

RO is mainly used in seawater and brackish water desalination, pure and ultrapure water production, separation and concentration of some liquids in food, beverage and chemical industries. A few sea water reverse osmosis desalination plants with the capacities of 500-2500m^3/d have been operated in different region. UF is mainly used in concentration of enzymes, proteins and other high molecular weight substances, and recovery of electrophoresis paints, as well as purification of water, beverages and other liquids. MF is found its uses in pharmaceutical industry and others for rejecting microparticles and bacteria from related liquids or gases. NF is used in water softening, purification and concentration of dye solution etc.

Performance of composite RO membranes and modules, typical performance of NF membranes and typical performance of NF elements are shown in Table 4, 5 and 6.

Table 4. Performance of composite RO membranes and modules

Membranes& modules	Performance		Test condition
	Flux/output	Rejection(%)	
Membrane	>40 (l/m2.h))	>98	1.6MPa <2000mg/l
Modules Φ100mm	>6.8m3/d	97—98	1.6MPa <2000mg/l

Table 5. Typical performance of NF membranes

Material	Solute Rejection (%)				
	NaCl	$MgSO_4$	Na_2SO_4	$MgCl_2$	Sucrose
PA	60	>98	>98	40	>98
SPES	50	40	>90	5	>40
CA	50	>90	---	---	---
CTA	55	>95	>95	---	---

Testing Conditions: 2000mg/l, 1.0MPa, 25°C

2.3 Emulsion Liquid Membranes

Study on emulsion liquid membranes was started in the end of 1970s. Since then important progress has been made both in the theoretical and practical aspects.

Theoretical studies include the mechanism on stability, swelling and breakdown of the emulsion, Synthesis of new effective surfactants, new emulsion liquid membrane systems, effect of frequency and wave pattern on breakdown emulsion by pulse electric field, supported emulsion liquid membranes, and electrostatic pseudo liquid membranes.

Abundant experiences have been obtained from some practical pilot systems. Following are some examples: removal of phenols, treatment of plating waste containing Cr or Zn, extraction and concentration of rare-earth elements, gold enrichment and recovery of cyanide and so on.

Table 6. Typical performance of NF elements

Material	Element	Performance		
		Flux (l/h)	NaCl Rejection(%)	$MgSO_4$ Rejection(%)
CA	SW100-1000	200	≤50	≥98
CTA	HF130-1300	700	≤50	≥98
PA	SW100-1000	480	≤30	≥95

Testing Conditions: 2000mg/l, 1.0MPa, 25°C

2.4 Dialysis and Artificial Kidney

Dialysis is now mainly used for recovery of acids. The hollow fiber used in artificial kidney has been studied and developed, but until now most of the hollow fiber are imported from Germany and Japan. Development of PES hollow fiber for artificial kidney has got good clinical result in recent years. Other related is blood filter and concentraters.

2.5 The Membranes in Chlor-Alkali Industry

From 1980 to 1990, the synthesis routes and technological process for preparing perfluorosulfonic and perfluorocarboxylic ion exchange resins had determined, tested in pilot scales, and the resins with high IEC and good strength were got also. The optimum technological parameters for membrane formations from the two resins and their mixture by extrusion had obtained. The manufacture of composite perfluorosulfonic and carboxylic membranes by vacuum technique in batch scale were also brought to success The transformation by hydrolysis and surface modification for large size of the membranes were also completed at same time.

2.6 Gas Separation Membranes

The study on gas separation membranes began in the end of 1970s. A great breakthrough has been made in N_2/H_2 separation and O_2 enrichment, and related demonstration applications have got good results also in the last 15 yeas.

Much work has been done on the research of membrane materials, such as the choose, synthesis and development of new materials, molecular design of the membrane materials, and related evaluation of their performance. The modified silicone rubber (PDMS), special polyimides, poly-4-methyl-1-pentene (PMP), brominated PPO, and poly-1-trimethylsilyl propyne (PTMSP) are examples of new materials.

PS hollow fiber resistant to high pressure, epoxy resin tube plate resistant to heat and pressure, and integral formation of composite layer in whole module have been developed for N_2/H_2 separation in recent years. The production of the hollow fiber module is in pilot scale, and the products have been used for H_2 recovery in fertilizer and refinery factories.

Reinforced PS supporting membranes, coating composite layer on the surface of the supporting membranes, technique for making spiral wound module and technological design for O_2 enrichment have also completed in recent years. The modules have being used for health protection and combustion supporting in glassworks.

The further improvement of the processes above, the research for N_2 enrichment and separating other gases, new membrane materials, hybrid processes and process optimization has also being carried out.

Table 7. Performance of different gas separation membranes

Type	Membrane	Module size	Performance**
Hollow fiber	PS hollow fiber coated with silicone rubber	ϕ50mm*3000mm ϕ100mm*3000mm ϕ200mm*3000mm	$\alpha_{H2/N2}$>25 J>400m^3/h(Φ100mm) J>1500m^3(Φ200mm)
Spiral wound	PS supporting membrane coated with silicone rubber	ϕ100mm*1000mm ϕ200mm*1000mm	$\alpha_{O2/N2}$=2 J>15m^3/h(Φ200mm)

** Performance depends on different condition

2.7 Inorganic Membranes

The characteristics of inorganic membranes are resistant to heat, chemicals and biological degradation. The methods for manufacture of inorganic membranes have been studied. These include the sol-gel process, anode-oxidation, coating and sintering, dynamically formed, and deposition etc. Ceramic (α-Al_2O_3) MF and UF membranes with 19 tunnels were successfully prepared and used in clarification and separation of liquids under harsh conditions. The other inorganic membranes are mainly used in high temperature reaction, such as hydrogenation and dehydrogenation.

Table 8. Performance of different inorganic membranes

Pore size (μm)	Supporting	Membrane	Flux(L/m^2.h)	Withstand Pressure(MP_a)	pH
0.05	Al_2O_3	Al_2O_3, ZrO_2, TiO_2	300~400	>1	0~14
0.2			800~900	>1	0~14
0.8			1100~1300	>1	0~14

2.8 Pervaporation

The study on pervaporation was started at the beginning of 1980s. The membranes used mainly were cross-linked PVA membrane, and PVA and chitosan alloy membrane. The other membranes, such as polyimide membrane and ion-exchange membranes, are also studied and tested. Synthesis of new membrane materials, small module design, manufactures and evaluation of the performance of the module and process optimization is also being proceeded.

Table 9. Performance of different PV membranes

Type	Performance		Test condition		
	Flux ($g/m^2.h$)	A	Feed concentration	Vacuum(mmHg)	Temperature(℃)
PV-1	120	1350	95%(wt) ethanol	2	70
PV-2	235	542	95%(wt) ethanol	2	70

2.9 New Membrane Processes

These processes include vapor permeation, membrane distillation, membrane extraction, membrane reactor, membrane phase separation, membrane electrode, affinity membrane and control release etc. Most of them now are still in their research and development stages.

Relatively low temperature requirement for membrane distillation is its major advantage. The PTFE, PP and PVDF strong hydrophobic membranes are used in the process. It is still in laboratory scale. The concentration polarization, temperature polarization and membrane infiltration are the main obstacles for the process and also the main research aspects. The process is tested in laboratory for saline concentration, juice concentration, recovery NH_3 from the waste of fertilizer factories, and Br_2 recovery from saline water etc. The osmotic distillation and osmotic membrane distillation are also studied in laboratory.

Scientists pay more attention to membrane reactor (MR) recent years, because one or more reaction products can be separated from reaction system, and the reaction rate and conversion rate can be raised significantly. More works have been down in membrane selection, immobilization of catalysts, transferring process and pilot experiment. MR is mainly tested in industrial chemistry and biochemistry, such as improvement and production of penicillin, fermentation and hydrogenation or dehydrogenation etc. MR has its promising future.

Study on affinity membrane was carried out in the beginning of 1990s. After basic research on materials, ligands and coupling etc, some affinity membranes were prepared and used in separation of endotoxin, and purification of γ-interferon.

Other membranes and processes, such as membrane extraction, membrane phase-separation, membrane electrode, control release, LB membranes and biological membranes etc. Have been also studied in their different stages.

3. Conclusion

The research development and application on membrane science and technology in China has got much progress since the beginning of 1960s, but the fundamental studies on membrane materials, mechanism of membrane formation and transport in membrane et al are very in sufficient. In order to lay a good foundation for further development, we should pay much attention to the fundamental research through the efforts of ourselves, and the international exchange and cooperation. At the same time, combining the research with application makes the research results get practical use quickly.

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