Conclusions

The mechanism of water dissociation in bipolar membranes can be rationalized by a hypothesis which postulates a catalytic reaction between a weak base and water. Based on this hypothesis, very stable chemical and thermal bipolar membranes can be prepared and operated efficiently at current densities in excess of 0.1 A cm^2. The process has many potential applications. There are, however, still a multitude of problems to be solved. Some are related to the poor selectivity of the bipolar membranes and poor acid-blocking capability of the anion exchange membranes; others are caused by the lack of application know-how and practical experience.

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Catalytic Membrane Reactors

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Introduction

The concept of completing both a reaction and separation in a single process unit has motivated research into the development of catalytic membrane reactors. For example, it has long been recognized that palladium metal has the capacity both to permeate hydrogen and to promote a variety of reactions. Thus, harnessing both of these features in a single device seemed a logical combination. In the mid 1960s, Wood and co-workers demonstrated that the dehydrogenation of cyclohexane to cyclohexene could be increased if the hydrogen produced was removed from the reaction vessel through semipermeable palladium walls. In this case, the palladium walls also acted to catalyse the dehydrogenation reaction. A membrane reactor of this type is illustrated in **Figure 1**.

In Russia, Gryaznov conducted much of the research that followed. Starting in the late 1970s, Gryaznov began publishing his results on the use of palladium membrane reactors both to produce and to recover hydrogen from a myriad of dehydrogenation reactions. In the dehydrogenation reactions, hydrogen leaves the reactor by permeating through the semipermeable membrane. However, reactors can also be used in reactions where hydrogen or other reaction products enter the reaction chamber by penetration through the membrane. The commonest classes of reactions that have been successfully influenced by the use of membrane reactor technology are listed in **Table 1**. Details relating to the large volume of research reported are provided in the Further Reading section. None of these membrane reactors are in commercial use. But some – the selective oxidation of methane, for example – are the subject of a very large industrial research effort. If successfully developed, this process would change the feedstock basis of a number of petrochemical processes.

Most research on the development of membrane reactors involves the use of these devices to shift equilibrium-limited reactions (often dehydrogenations). The thermodynamic equilibrium of the reactants and products at the temperature and pressure of the reaction determine the conversion achievable in any given reaction. For dehydrogenation reactions, increasing temperature and decreasing pressure promote an enhanced reaction. Unfortunately, each of these solutions has an associated cost. Increasing the reaction temperature typically results in a reduced

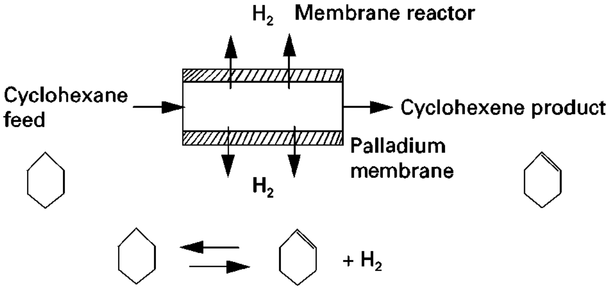

Figure 1 Schematic of a membrane reactor using hydrogen-permeable palladium membranes to shift the equilibrium of the dehydrogenation reaction cyclohexane to cyclohexene.

Table 1 Reaction classes that may be amenable to membrane reactor technology

Reaction class	*Example*	*Role of membrane*
Hydrogenation	$C_2H_2 + H_2 \rightarrow C_2H_4$ in presence of C_2H_4	Controlled addition of hydrogen
Hydrogenolysis	Cyclopentadiene $+ H_2 \rightarrow$ cyclopentene + cyclopentane	Controlled addition of hydrogen
Dehydrogenation	Cyclohexane $\rightarrow$ benzene $+ {}^3H_2$	Remove hydrogen to shift equilibrium limitation
Partial oxidation	Butane $+ O_2 \rightarrow$ maleic anhydride	Recovery of intermediate product of control reactant at addition rate to promote formation of intermediate product
Esterifications	$R\text{–}OOH + CH_3OH \rightarrow R\text{–}O\text{–}O\text{–}CH_3 + H_2O$	Selective water removal to shift equilibrium limit without loss of reactant
Syn gas	$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$	Selective oxidation of methane
Oxidative coupling	$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O$	Selective oxidation of methane

catalytic selectivity for the desired product. Reducing pressure comes at the cost of adding a diluent to the reactor, paying for the additional capital to handle this component and paying the price of downstream separation.

Figure 2 provides a schematic representation of the behaviour of a conventional reactor and a theoretical membrane reactor. The conventional data are for a highly active butane dehydrogenation catalyst operating at 1 atm total pressure (pure normal butane feed). In the conventional system, the selectivity of the catalyst degrades rapidly at temperatures that are just beginning to promote reaction. Thus, the catalytic yield (defined as the product of conversion and catalytic selectivity) goes through a pronounced maximum. Incorporation of an appropriately designed membrane into the reactor system results in the removal of hydrogen from the system. The catalytic selectivity does not appear to be influenced by this process, but the conversion of butane to butene is enhanced by the reduction in the hydrogen partial pressure. Thus, the yield of the membrane reactor system is markedly improved.

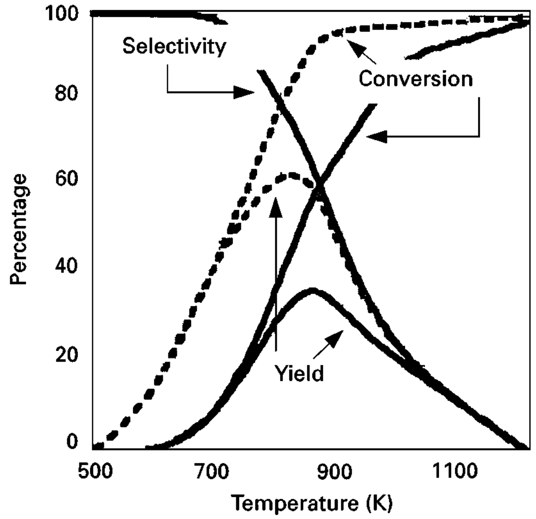

Figure 2 Influence of product hydrogen removal on the dehydrogenation of butane. Based on pure butane feed with 1.1 atm total pressure. Continuous line, conventional reactor; dashed line, membrane reactor.

The ability to operate at acceptable conversions while maintaining very high catalytic selectivity is a strong driving force for the use of membrane reactor technology. By operating in a high selectivity region, the production of by-products that can act as catalyst poisons is minimized. This results in a longer catalyst life between regenerations and reduced waste production.

Possible Membrane Configurations

Incorporation of a reaction and separation zone in a single process unit allows for a variety of possible configurations. The optimum design of the equipment is closely tied to the reaction conditions and the ability of the membrane material to serve as a catalyst. Several of the more common configurations are shown in **Figure 3**. For illustrative purposes, the dehydrogenation of a compound to form hydrogen will be considered. The hydrogen is removed from the reaction zone to increase the equilibrium conversion. Similar configurations can be employed for the other reactions listed in Table 1. As described below, these configurations represent the most frequently employed designs, however, the list is not exhaustive and new configurations are developed and patented regularly.

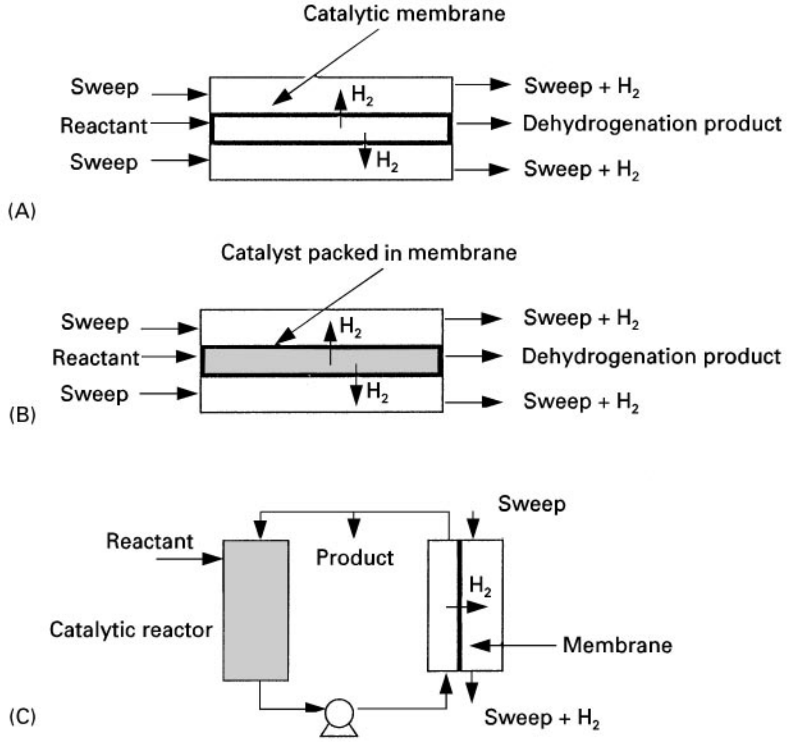

Figure 3 Common membrane reactor configurations. (A) Catalytic membrane; (B) membrane tube packed with catalyst; (C) membrane-assisted batch reactor.

Catalytic Membrane

One of the earliest catalytic membrane configurations employed was that of the reactive tube. In this configuration, the material used to construct the tube fulfils both the roles of separation medium and catalyst. Few materials have this special capability. Palladium is one. Palladium has the ability to transport hydrogen through the matrix by a process of adsorption, dissociation, diffusion, and then reassociation on the low pressure side. Palladium is also a reasonable catalyst for many of the reactions detailed in **Table 1**, especially hydrogenation and dehydrogenation reactions. Thus, using this material to achieve both functions was an obvious consideration.

Transport can only be achieved through a chemical potential driving force of the hydrogen from the reaction zone to the separation zone. Such a driving force has been established with the use of a sweep gas on the permeate side to keep the hydrogen concentrations low. The sweep gas may either be inert or reactive with the hydrogen. Inert sweep gases offer the advantage of being simple to employ. Unfortunately, to achieve a partial pressure difference across the membrane, the sweep gas rate must be high and the permeated hydrogen is recovered as a dilute component in the sweep gas.

Reactive sweep gases offer other engineering possibilities and challenges. The use of air as a sweep gas in catalytic dehydrogenation membrane systems has been reported. At dehydrogenation temperatures (300–600°C), oxygen can react with hydrogen to form water. This reaction is highly exothermic. In contrast, the dehydrogenation reaction is endothermic. Thus, thermal matching of the heat released by the hydrogenation of oxygen and the heat consumed by the dehydrogenation reaction would allow for an isothermal system. Because the hydrogenation reaction is rapid, the effective partial pressure on the permeate side of the membrane can be maintained near zero.

Catalytic membrane systems require that the membrane material be stable for both reaction and separation and that it operates well in both modes simultaneously.

Packed Tube

Optimization of a single material for both catalytic and separative functions is challenging. Few materials have the ability to transport the desired component and act as a catalyst for the desired reaction. Furthermore, even for materials that possess both characteristics, precise matching of the rates of reaction and transport is difficult. To overcome these limitations, a packed membrane tube configuration has been employed. In such a configuration, a catalyst is packed in the bore of a tubular membrane. Reactants are fed into the catalyst zone and products have the potential to be transported through the membrane walls and out of the reaction zone. This configuration offers tremendous flexibility in the selection of the catalyst and membrane to be used. Both homogeneous and heterogeneous catalysts have been employed in this configuration.

Membrane-assisted Batch Reactor

The membrane-assisted batch reactor is most frequently considered for implementation because it requires the smallest process modification from traditional catalytic reactors. In this configuration, a membrane unit is added in the recycle line of a batch reactor. In so doing, the membrane has the capacity to selectively remove a product component or to selectively add a reactant. It has the advantage of allowing the pressure or temperature of the membrane and reactor unit to be controlled independently. Therefore, the properties of the membrane can be varied to optimize the separation achieved.

Membrane-assisted configurations suffer from the inability to remove product components completely as they are produced. This limits the conversion to values that are lower than those that are theoretically possible in the other configurations considered.

Available Membranes

The development of catalytic membrane reactors is limited by the availability of membranes capable of controlling the reaction environment that are stable at reaction conditions. A brief review of transport through membranes is provided and then the additional membrane requirements are summarized. **Figure 4** provides a schematic of a membrane employed for the transport of a gaseous component.

Transport of a component through a solid is only possible if there are differences between the chemical potential of the component on the two faces of the solid. For gas-phase systems that operate at moderate pressures and can be considered to be ideal, transport can be described by:

$$\mathrm{Flux}_{\mathrm{i}} = P_{\mathrm{i}}(p_{\mathrm{Hi}} - p_{\mathrm{Li}})/l \qquad [1]$$

where P_{i} is the permeability of component i through the membrane, p_{Hi} is the partial pressure of component i on the high pressure side, p_{Li} is the partial pressure of component i on the low pressure side and ℓ is the membrane thickness.

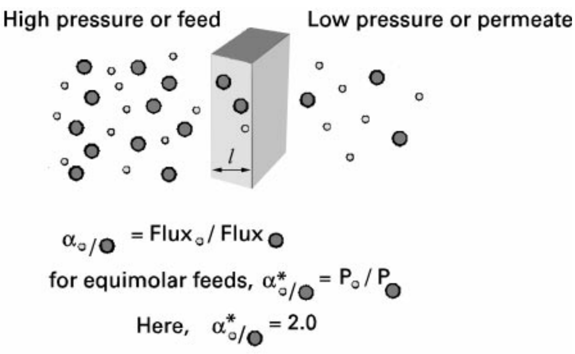

Figure 4 Schematic of transport through a solid.

Thus, the difference in the partial pressure of the component to be transported controls the rate of transport. A high partial pressure driving force can be produced through:

- high total pressure on the feed side
- high concentration of the component of interest on the feed side
- low total pressure on the permeate side (using a vacuum)
- very low concentration of i on the permeate side using a very high dilution ratio of sweep gas

The rate at which a component is transported through a solid is defined as the flux of the component, (eqn [1]). To facilitate the comparison of a variety of materials, the properties of the material (permeability) have been separated from the process conditions (membrane thickness, pressures and concentrations). For equivalent process conditions, the material with the highest permeability will have the fastest transport.

The selectivity of a membrane for any pair of gases (A, B) is usually defined by the term $\alpha_{\mathrm{A/B}}$, equal to the ratio of the gas permeabilities:

$$\alpha^*_{\mathrm{A/B}} = P_{\mathrm{A}}/P_{\mathrm{B}} \qquad [2]$$

For membrane reactors, membranes with high selectivities are required, so only the required component enters or leaves the reactor.

Specific Membranes

Certain materials have the ability to transport a single component with the complete exclusion of all others. Transport of hydrogen and oxygen through two of these materials is reviewed here.

Metals (hydrogen) Palladium and some of its alloys have the ability to transport hydrogen while completely excluding all other compounds. The permeation of hydrogen through metals is a multistep process involving:

- chemisorption of hydrogen on to the metal surface
- dissociation of the hydrogen
- dissolution of the atomic hydrogen from the surface into the bulk of the metal
- diffusion across the metal layer
- the desorption from the bulk of the metal to the surface
- reassociation
- desorption of molecular hydrogen from the metal surface

The diffusion of atomic hydrogen across the metal layer is typically the rate-limiting step. Therefore, the transport of the hydrogen can be modelled using a Fickian diffusion equation.

Alloys of palladium have proven effective for the transport of hydrogen. Pure palladium undergoes a phase transformation in the presence of hydrogen at moderate temperatures, and a density change ensues. Even though these changes are small, they are sufficient to produce a brittle, cracked and nonselective material after only a few cycles. Therefore, few of the membranes evaluated are pure palladium and most commercial metallic hydrogen purifiers are prepared from a palladium/silver alloy containing 23% silver.

A significant limitation to the use of palladium membranes is their strong susceptibility to poisoning by sulfur compounds and CO compounds frequently found in the hydrocarbon streams of interest. Research into the development of more resistant materials is underway. However, the improved resistance has so far been attained at the cost of permeability. This issue must be resolved before these membranes can be used in the chemical process industry.

Nonporous ceramics (oxygen) Ceramic membranes have been developed which will selectively transport hydrogen or oxygen. Hydrogen has been shown to be transportable through nonporous silicon dioxide. While the transport rates are extremely slow, the selectivity to hydrogen transport is infinite, just as in defect-free palladium. Silicon dioxide has the advantage of being more resistant to the presence of sulfur compounds that act as poisons for palladium. Nevertheless, the challenge of forming this material into extremely thin layers has limited its use. Perhaps as preparation techniques continue to improve, the use of this material for the highly selective transport of hydrogen will be re-examined.

Nonporous ceramics have also been used for the transport of oxygen. Oxide-conducting materials, including stabilized zirconia, have been used in membrane reactors. These membranes can successfully transfer oxygen while barring the transport of all other compounds. Current limitations relating to the temperatures required for operation are discussed in subsequent sections.

Nonspecific Membranes

Commercial utilization of membranes has relied almost exclusively on the use of nonspecific membrane materials. These materials have the ability to transport one component of a gas mixture in preference to a second. However, they are permeable to all components to at least some degree. Therefore, unlike palladium, which can act as a perfect separator, these membranes transport all stream components. The properties of both porous ceramics and polymeric membranes will be considered here.

Porous ceramics Porous ceramic membranes, with pore sizes ranging from a few nanometers to several microns, have been produced and are commercially available. These membranes separate by size exclusion. For the separation of gases and low molecular weight liquids, Knudsen diffusion is typically employed. For gases, Knudsen diffusion occurs for pore sizes of about 4–100 nm. For systems operating under the Knudsen diffusion regime, the separation of two molecules can be defined as:

$$\alpha_{A/B} = (MW_B/MW_A)^{0.5} \qquad [3]$$

Thus, high degrees of separation selectivity are only possible if the molecular weight difference between the two components is large. These materials have been employed for the separation of hydrogen from hydrocarbon streams. The ideal separation selectivity for hydrogen over butane, for example, is 5.8. Thus, a small but measurable separation can be achieved.

The microporous nature of these membranes allows them to have very high transport rates, as compared to nonporous palladium or ceramic materials. Yet, the separation achievable is limited.

Polymers The final category of membrane materials to be considered is polymers. Polymeric membranes are employed for the separation of gas streams, the recovery of organic vapour from air, the separation of mixtures of organic liquids and filtration of particles from aqueous streams. Nonporous polymeric membranes have been considered for membrane reactor applications. Nonporous polymeric membranes separate on the basis of sorption of the component into the polymeric matrix, diffusion across and desorption from the low pressure side.

Polymers offer several advantages when compared with the porous ceramics. For many gas pairs, the inherent selectivity of the polymeric membrane is substantially higher than that of a Knudsen diffusion-controlled ceramic. The polymeric membranes are also easier to prepare in high surface per volume modular configurations, resulting in a considerably lower price. Recent estimates put the price of commercial polymeric membranes at well under $10 per square foot membrane area, installed. In contrast, ceramics may cost 10 times as much.

Many applications of membrane reactors, including dehydrogenation of hydrocarbons, hydrogenations and partial oxidation reactions are high temperature reactions. Conventional polymeric membranes do not have either the chemical or thermal stability to be successfully used in these reactions. However, recent advances have provided materials that can be processed using conventional solvent-based techniques and are later cross-linked to provide the chemical and thermal resistance necessary for membrane reactor applications. New polyimide-based materials provide such characteristics.

Polyimides that are thermally stable to 300°C for extended periods have been reported. When incorporated in a membrane reactor for the dehydrogenation of butane, the system performance increased markedly. With no membrane, conversions of 22% were achieved. Following addition of the membrane to the integrated system, the conversion increased to over 30%.

The development of chemically stable polymeric materials provides an opportunity to influence liquid-phase organic reactions.

Applications

While the use of membranes to influence catalytic reactions has been explored in great detail, few systems have been employed commercially. Some of the possible reasons for this slow adoption are listed below. Nevertheless, a few materials are produced through the use of membrane reactor technology. Gryaznov, for example, has reported the production of vitamin K using a single-step process utilizing a membrane reactor. The membrane was employed to control the hydrogenation of a mixture of quinone and acetic anhydride to form vitamin K. The membrane reactor process resulted in a 95% yield using an external hydrogen pressure of 1 atm. The conventional process required several processing steps and resulted in only 80% yield. This membrane reactor process is reported to be employed commercially in Russia.

Current Limitations

Some of the more important technical issues that have limited the implementation of membrane reactor technology are detailed below. In addition to technical problems, economic considerations are a concern. For many of the systems considered (Table 1), commercial production facilities using conventional reactor technology are available. If membrane reactors are to supplant these existing systems, the economic benefit must be substantial. Furthermore, the cost of the membrane reactor system must be only marginally higher than the conventional system. For most reactions, this is not currently the case.

Need for Pressure Drop

When one considers the use of membrane reactor technology for the selective removal of a product component (such as in dehyhdrogenations), the design of the membrane will be governed by the need for a partial pressure difference of this component. To increase the equilibrium conversion, these systems are run at low pressure with a goal of complete removal of the component as it is produced. Thus, the partial pressure of the product component is nearly zero in the reaction zone. For transport to occur, the partial pressure on the permeate side must be lower. Several techniques have been employed to attain partial achievement of these goals. These include high volumes of sweep gas on the permeate side; vacuum on the permeate side; and transforming the system to a batch reactor with continuous removal of the product component. In the last case, the partial pressure on the feed side is maintained at some finite level, and additional conversion is achieved by long residence times.

Sweep gas The use of high sweep gas ratios (nitrogen or argon is commonly employed in the laboratory) is effective in reducing the partial pressure of products in the reaction zone and enhancing conversions. For nonspecific membranes, it has been shown that two processes reduce the partial pressure of products: transport of the product from the reaction zone to the separation zone, and transport of sweep gas from the separation zone to the reaction zone. This latter process can occur because the membrane is nonselective and the partial pressure gradient of the sweep gas drives the transport. As the sweep gas permeates into the reaction zone, it acts as a diluent and provides a mechanism for an increase in the percentage conversion in the reactor. Unfortunately, the downstream separations required in these systems are significant and the economics are less favourable than simply mixing the diluent with the reactants in a conventional reactor.

Vacuum permeate An alternative method to produce a pressure drop is the use of a vacuum on the membrane permeate. This has been shown to be highly effective in laboratory settings. However, the economics are not favourable for the large scale production of inexpensive components. Nevertheless, vacuum permeate systems may prove viable for small, high value-added systems.

Batch versus continuous Continuous reactor systems are preferred; they require less down time and have higher production rates than batch systems of similar size. However, as previously detailed, if the role of the membrane is to remove a product component, the available partial pressure difference is limited and the process will always be working with a very limited pressure drop that will require very large membrane areas. Batch and semi-batch processes allow the system to develop some limited partial pressure difference before membrane separation is attempted.

Membrane Degradation

The stability of the membrane is another important consideration. Ideally, for integrated systems, the membrane should be stable in all possible reaction environments: catalyst activation, normal reaction, catalyst regeneration and any thermal cycling experienced upon transitions. This presents specific challenges for each system and there are few materials that can satisfy all of these requirements. Thus, special engineering solutions are necessary. Even if the membrane material can fulfil these specifications, the many components needed to produce a membrane reactor module may not.

Future Possibilities

Organic Separations

A great deal of research is currently focusing on the development of membranes (either polymeric, inorganic, or hybrids of the two) for the selective separation of liquid organic mixtures. If this research is successful, it will allow for incorporation into liquid-phase membrane reactors.

Control of Reactant Addition for Intermediate Product Recovery

A second area of immense current research activity is the development of oxygen-permeable membranes to influence the conversion of methane to either methanol or syn gas. The goal in these processes is a mechanism for the conversion of natural gas to a transportable liquid that may be further converted to high valued products. Current research has shown that membranes can be developed and that the appropriate catalysts are available for these conversions. Many engineering challenges lie ahead. These membrane reactor processes operate in excess of 700°C (sometimes much higher). Sealing these ceramic membranes into a housing remains a limitation. Further, the thermal stresses, which develop when cycling from 25 to > 700°C, may result in membrane damage. While these are complex problems, the incentive to succeed is large and numerous research efforts continue in this area.

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Concentration Polarization

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Introduction

All membrane separation processes are accompanied by a phenomenon called ‘concentration polarization’ in which the composition at the feed–membrane interface differs from the composition in the bulk of the feed mixture. This gradient in composition is generated by the separation performed by the membrane and, as such, cannot be avoided. However, it is important to minimize the effects of concentration polarization because the gradient in composition reduces the separation performance of the membrane and increases the potential for membrane fouling.