supersaturation under a partial pressure gradient, and (ii) to promote heterogeneous nucleation on the membrane surface, so decreasing the energy barrier to the formation of critical nuclei and, ultimately, accelerating the crystallization process, has been clearly envisaged for the first time by Curcio *et al.* (2001).[2]

In principle, several membrane operations can be used to drive a solution to supersaturation by selective removal of solvent. Hybrid processes based on pressure-driven membrane operations, such as nanofiltration (NF) or reverse osmosis (RO) are used to concentrate an aqueous solution by removing the solvent in liquid phase while retaining the solute; crystals are then recovered in a separate tank often operated at lower temperature and with seeding.[3,4] However, due to the progressive increase of osmotic pressure at high concentration, exacerbated by concentration polarization phenomenon, these membrane-assisted operations are limited to the recovery of sparingly soluble salts.[5]

In addition, a solid product can be formed by reactive crystallization as a result of active or passive diffusion of reactants through a membrane. Takiguchi *et al.* (2006) investigated the reactive crystallization of $CaCO_3$ promoted by the use of ion exchange membranes for a selective transport of $CaCl_2$ and $NaCO_3$.[6] It was observed that calcium carbonate crystals grew in the form of tube-structured agglomerates (self-assembled calcite microcrystals) on the surface of a Nafion N-117 cation-exchange membrane within a sodium carbonate solution.

Ye *et al.* (2013) investigated the crystallization of Na_2CO_3 by reactive absorption of CO_2 into alkaline NaOH solution by using a gas–liquid membrane contactor.[7] The membrane is microporous and hydrophobic, not wetted by the polar phase; carbon dioxide, diffusing through the membrane, reacts with hydroxyl ions leading to the formation of HCO_3^- and CO_3^{2-} species.

In this chapter the attention is focused on three membrane crystallization configurations which promise applicability to a wide variety of crystallization processes from solutions:

1. Temperature-driven membrane crystallization, in which supersaturation is generated by the transmembrane evaporation of solvent from the warm feed side to the opposite side (distillate), taking place under a vapour pressure gradient generated by a temperature difference;
2. Osmotic-driven membrane crystallization, in which supersaturation is generated by the transmembrane evaporation of solvent from the feed solution taking place under a partial pressure gradient promoted by a concentration difference, often generated by a hypersaline (draw) solution kept at the same temperature as the feed solution;
3. Antisolvent membrane crystallization, in which an antisolvent is transferred in vapor phase to the crystallizing solution across a membrane, according to the same principle described in 1).