

which has a water contact angle generally of between 144° and 149° with an example at $150.6^\circ \pm 0.4^\circ$.

C. Y. Kuo *et al.*, Desalination: 233 (2008) 40-47, studied the precipitation of a solution of PVDF/NMP in light alcohols such as methanol, ethanol, n-propanol and n-butanol. It was demonstrated that the precipitation using a single bath of alcohol results in highly hydrophobic membranes having a water contact angle ranging from 144° (for methanol) up to 148° for n-propanol. The morphology obtained is bi-continuous. The use of the precipitation with the aid of a dual bath, firstly in alcohol (2 s) then in water, gives membranes having a bi-continuous morphology but with a smaller contact angle (136° for n-propanol).

Q. Li *et al.*, Polym. Adv. Technol. DOI: 10.1002/pat.1549 (2009) themselves describe three other routes for preparing PVDF membranes that are highly hydrophobic (maximum water contact angle 136.6°):

- from a solution of PVDF in a TEP/DMAc mixture, a step of evaporation of 60 min is applied in a relative humidity of 60% followed by a precipitation in water. A morphology of frisée lettuce leaf type is obtained, having a weak interconnection;
- by precipitation in ethanol, the same morphology is obtained in the bulk of the membrane but a rough and dense layer is obtained at the surface;
- the precipitation in a dual bath (the first composed of a greater or lesser proportion of solvent, followed by a second bath of water) makes it possible to increase the surface porosity without losing the mechanical strength. However, the morphology remains that of "frisée lettuce" with a maximum water contact angle of 136.6° .

The objective of the ~~embodiments disclosed herein~~^{present invention} is to prepare superhydrophobic PVDF membranes. These membranes are porous and have a hierarchized surface morphology. The porosity of the membrane, combined with a two-fold level of organization, on the micrometric scale and on the nanometric scale, is capable of trapping air and makes it possible to generate superhydrophobic surface properties also known under the name of the lotus effect. This is an approach inspired by structures encountered in nature (biomimetism) on lotus leaves and the feet of water measurers (*Hydrometra stagnorum*). By using the VIPS process described above, it has not been possible to prepare PVDF membranes that are mechanically stable and suitable for industrial applications. Specifically, in this case, the crystalline nodules are not interconnected. It is therefore desirable to prepare PVDF

membranes having a hierarchical structure of crystalline nodules, the surface of which has a porous structure on the nanometric scale (100 to 600 nm) and the nodules of which are interconnected (structure also referred to as “nanostructured morphology”).

For this purpose, ~~and according to a first aspect~~, one subject of the ~~disclosureinvention~~ is a PVDF membrane comprising a superhydrophobic surface comprising a porous structure on the nanometric scale and interconnected crystalline nodules of micrometric size. Characteristically, said superhydrophobic surface has a water contact angle of greater than or equal to 150° . The contact angle is measured by depositing an 8 μ L drop of water under ambient temperature ($21 \pm 3^\circ\text{C}$) and pressure conditions. The value indicated is an average of at least 4 independent measurements.

In a first aspect, there is provided a polyvinylidene fluoride membrane comprising a surface having a water contact angle of greater than or equal to 150° , said contact angle being measured under ambient temperature ($21 \pm 3^\circ\text{C}$) and pressure conditions, and said surface comprising interconnected crystalline nodules having a size of between 5 and 12 micrometers.

~~According to a second aspect, the disclosure alsoinvention~~ relates to a process for preparing the superhydrophobic PVDF membrane according to the invention, comprising a precipitation operation from an alcohol-water dual bath system.

In a second aspect, there is provided a process for manufacturing the polyvinylidene fluoride PVDF membrane as defined herein, said process comprising the following steps: a. dissolving an amount of PVDF in a solvent at a temperature of at least 60°C , said solvent being used with the addition of water at between 3% and 5% by weight with respect to the weight of the solvent; b. spreading the PVDF solution thus obtained onto a solid support in order to form a film on the surface of said support; c. immersing said film in a first bath containing an alcohol chosen from methanol, ethanol, n-propanol, isopropanol and n-butanol, for a duration of greater than or equal to 1 minute, preferably greater than or equal to 5 minutes; then d. immersing said support in a second bath of water.

In a third aspect, there is provided the use of a membrane as defined herein or capable of being obtained by the process as defined herein, for the distillation of water.

In a fourth aspect, there is provided the use of a membrane as defined herein or capable of being obtained by the process as defined herein, as a filtration membrane.

In a fifth aspect, there is provided the use of a membrane as defined herein or capable of being obtained by the process as defined herein, in a lithium battery.

The ~~disclosure~~invention and the advantages that it provides will be better understood in light of the detailed description which follows and the appended figures in which:

- figure 1 illustrates the membranes prepared in example 1;
- figure 2 illustrates the membranes prepared in example 2;
- figure 3 illustrates the membranes prepared in example 3;
- figure 4 illustrates the membranes prepared in example 4;
- figure 5 illustrates the membranes prepared in example 5;
- figure 6 is the image obtained by scanning electron microscopy (SEM) of a superhydrophobic membrane according to the invention obtained by precipitation of the PVDF in an isopropanol-water dual bath;
- figure 7 illustrates the structure of several membranes observed using SEM, prepared by the VIPS process and by precipitation of PVDF in a dual bath of: methanol-water; ethanol-water; n-propanol-water; isopropanol-water; 1-butanol-water; 1-octanol-water and 1-decanol-water, respectively.

Hydrophobic PVDF membranes are employed on a grand scale owing to their multiple qualities: hydrophobicity, heat resistance, chemical resistance, resistance to UV radiation, etc. PVDF is a semicrystalline polymer containing a crystalline phase and an amorphous phase. The crystalline phase confers good heat stability, whereas the amorphous phase confers flexibility on the membranes manufactured from this polymer. It is desirable to have PVDF membranes for which certain properties have been further improved. One route developed over recent years aims to increase the hydrophobicity properties of PVDF