As the first true RFB, the Iron-Chromium redox flow battery (ICRFB) is very attractive in terms of its cost effectiveness, comprising cheap and abundant active materials. It has a standard overall cell potential of 1.18 V with the reactions occurring within the battery are listed below.

Positive Electrode: $Fe^{2+} \rightleftarrows Fe^{3+} + e^{-}$ $E^0 = +0.77V$ (1)

Negative Electrode: $Cr^{3+} + e^{-} \rightleftarrows Cr^{2+}$ $E^0 = -0.41V$ (2)

Overall: $Fe^{2+} + Cr^{3+} \rightleftarrows Fe^{3+} + Cr^{2+}$ $E^0 = +1.18V$ (3)

Despite the cost effectiveness of the ICRFB, it is prone to significant membrane crossover of the active species that results in irreversible capacity decay. This same capacity occurs for many other inexpensive RFB chemistries and has largely prevented their commercialization.

There is still a need for a selective sol-gel membrane that can reduce flow battery costs and enable new flow battery chemistries.

SUMMARY

This summary is provided to introduce a selection of concepts in a simplified form that are further described below in the Detailed Description. This summary is not intended to identify key features of the claimed subject matter, nor is it intended to be used as an aid in determining the scope of the claimed subject matter.

There is provided a nanoporous selective sol-gel ceramic membrane, generally including a porous support having a plurality of support pores that are 10 nm or greater in diameter; and a nanoporous composite comprising a nanoporous sol-gel ceramic composite filling at least a portion of the porous support; wherein the nanoporous composite comprises a plurality of nanopores of 5 nm or smaller in radius with a polydispersity index of 0.7 or lower.

In an aspect, the present disclosure provides a nanoporous ceramic membrane, comprising: a porous support having a plurality of support pores that are 10 nm or greater in diameter; and a nanoporous composite comprising a nanoporous ceramic filling at least a portion of the plurality of support pores; wherein the nanoporous ceramic has a spherical fractal nanoporous

structure as determined by fitting small-angle scattering spectra of the nanoporous ceramic to a mathematical model.

There is also provided a selective-membrane structure generally including a plurality of individual selective membranes joined in a planar configuration.

DESCRIPTION OF THE DRAWINGS

The foregoing aspects and many of the attendant advantages of this invention will become more readily appreciated as the same become better understood by reference to the following detailed description, when taken in conjunction with the accompanying drawings, wherein:

FIGURE 1 illustrates a method, in accordance with an embodiment of the disclosure, for preparing an exemplary nanoporous selective sol-gel ceramic composite membrane. Step 1: Apply edging to support. Step 2: Sol-gel coating from precursor solution.

FIGURE 2 illustrates a method, in accordance with an embodiment of the disclosure, for preparing an exemplary nanoporous selective sol-gel ceramic composite membrane. Step 1: Apply edging. Step 2: Pre-coating containing performance enhancing materials. Step 3: Sol-gel coating from precursor solution.

FIGURE 3 illustrates a method, in accordance with an embodiment of the disclosure, for preparing an exemplary nanoporous selective sol-gel ceramic composite membrane. Step 1: Apply edging. Step 2: Sol-gel coating from precursor solution. Step 3: Dip in an acid or salt bath to induce further gelation.

FIGURE 4 is a schematic illustration of an H-Cell setup with $CrCl_3$ on side 1 and $AlCl_3$ on side 2 or $VOSO_4$ on side 1 and $MgSO_4$ on side 2.

FIGURE 5 is a schematic illustration of a 4-electrode PEIS setup.

FIGURE 6 is a graph of extrinsic permeability of Cr^{3+} ions through Nafion® membranes and nanoporous selective sol-gel ceramic composite membranes, in accordance with an embodiment of the disclosure.

FIGURE 7 is a graph of extrinsic permeability of Fe^{3+} ions through Nafion® membranes and nanoporous selective sol-gel ceramic composite membranes, in accordance with an embodiment of the disclosure.

CLAIMS

1. A nanoporous ceramic membrane, comprising:

a porous support having a plurality of support pores that are 10 nm or greater in diameter; and

a nanoporous composite comprising a nanoporous ceramic filling at least a portion of the plurality of support pores;

wherein the nanoporous ceramic has a spherical fractal nanoporous structure as determined by fitting small-angle scattering spectra of the nanoporous ceramic to a mathematical model.

2. The nanoporous ceramic membrane of claim 1, wherein the mathematical model is a fractal aggregate model.

3. The nanoporous ceramic membrane of claim 2, wherein a least squares regression fit of a de-smeared, 1-dimensional small-angle scattering spectra to the fractal aggregate model provides a χ^2/N_{pt} value of less than 10,

wherein

χ^2 is a sum of an intensity difference between the fractal aggregate model and small-angle scattering spectra data, and

N_{pt} is a number of small-angle scattering data points over a model fitting range.

4. The nanoporous ceramic membrane of claim 2, wherein the fractal aggregate model is a measure of scattering intensity, I, as a function of a scattering vector, q, according to the equation:

$$I(q) = P(q)S(q) + bck$$

wherein

P(q) is a form factor of building blocks of the fractal aggregate model,

S(q) is an effective structure factor of the fractal aggregate model, and

bck is background scattering.

5. The nanoporous selective ceramic membrane of claim 4, wherein

the form factor, P(q), is a homogenous spherical form factor defined by the equation

$$P(q) = scale \times V(\rho_{block} - \rho_{solvent})^2 F(qR_0)^2,$$

$$F(x) = \frac{3[\sin(x) - x\cos(x)]}{x^3},$$

$$V = \frac{4}{3}\pi R_0^3,$$

$$S(q) = 1 + \frac{D_f \Gamma(D_f - 1)}{[1 + 1/q\xi)^2]^{(D_f - 1)/2}} \frac{\sin[(D_f - 1)\tan^{-1}(q\xi)]}{(qR_0)^{D_f}},$$

scale is a volume fraction of building blocks of the measured nanoporous sol-gel ceramic,

R_o is a radius of the building blocks,

D_f is a fractal dimension,

ξ is a correlation length,

$\rho_{solvent}$ is a scattering length density of a solvent, and

ρ_{block} is a scattering length density of the building blocks.

6. The nanoporous ceramic membrane of claim 1, wherein the surfaces of the nanoporous ceramic are coated with a coating comprising an alkyl group.

7. The nanoporous selective ceramic membrane of claim 1, wherein the scattering

intensity is fit to the mathematical model over a scattering vector, q, range of about 0.01 $Å^{-1}$ to about 1 $Å^{-1}$.

8. The nanoporous ceramic membrane of claim 5, wherein scale corresponds to a membrane porosity when the small-angle scattering spectra is in intensity units of 1/cm and is less than 0.7.

9. The nanoporous selective ceramic membrane of claim 5, wherein the fractal dimension, D_f, is constrained to a range of about 1 to about 3.

10. The nanoporous ceramic membrane of claim 5, wherein

$\rho_{solvent}$ is defined by a scattering length density of a material of a solvent in the selective sol-gel ceramic membrane, and

ρ_{block} is defined by a scattering length density of a material of the building blocks.

11. The nanoporous selective ceramic membrane of claim 4, wherein bck is allowed to vary during fitting.

12. The nanoporous selective ceramic membrane of claim 1, wherein the small-angle scattering spectra includes small-angle scattering spectra selected from the group consisting of small-angle x-ray scattering spectra, small-angle neutron scattering spectra, small-angle light scattering spectra, and combinations thereof.

13. The nanoporous selective ceramic membrane of claim 1, wherein the mathematical model has a polydispersity ratio in a radius parameter.

14. The nanoporous ceramic membrane of claim 13, wherein the polydispersity ratio is constrained to less than 0.7.

15. The nanoporous ceramic membrane of claim 13, wherein the polydispersity ratio is from a log-normal distribution.

16. The nanoporous ceramic membrane of claim 1, wherein the small-angle scattering spectra of the nanoporous ceramic are measured after rinsing and drying the nanoporous ceramic to remove residual liquid and contaminants.

17. The nanoporous ceramic membrane of claim 1, wherein the nanoporous ceramic comprises oxygen in a range of about 20 mole % to about 80 mole %.

18. The nanoporous ceramic membrane of claim 17, wherein the nanoporous ceramic comprises a material selected from the group consisting of silica, alumina, titania, zirconia, germania, and combinations thereof.

19. The nanoporous ceramic membrane of claim 1, wherein the nanoporous ceramic has a porosity volume fraction in a range of about 0.01 to about 0.7.