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.

~~In one aspect, the present disclosure provides~~ 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 ~~another~~ an aspect, the present disclosure provides a nanoporous ~~selective sol-gel~~ ceramic membrane, ~~generally including~~ 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 ~~sol-gel~~ ceramic ~~composite~~ filling at least a portion of ~~an active area of~~ the plurality of ~~porous~~ support pores; wherein the nanoporous ~~sol-gel~~ ceramic has a spherical fractal nanoporous

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

~~In yet another aspect, the present disclosure provides a~~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

~~The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:~~

~~1. A nanoporous selective sol-gel 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 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.~~

~~2. The nanoporous selective sol-gel ceramic membrane of Claim 1, wherein the porous substrate comprises a material selected from the group consisting of a polymeric material, a ceramic material, a metal, and a combination thereof.~~

~~3. The nanoporous selective sol-gel ceramic membrane of Claim 1, wherein the porous substrate comprises a material selected from the group consisting of polypropylene, polyethylene, polyvinyl chloride, polystyrene, polyamide, polyimide, polyacetonitrile, polyvinylacetate, polyethylene glycol, poly ether ketone, polysulfone, polysulfonamide, polyacrylamide, polydimethylsiloxane, polyvinylidene fluoride, polyacrylic acid, polyvinyl alcohol, polyphenylene sulfide, polytetrafluoroethylene, cellulose, and combinations thereof.~~

~~4. The nanoporous selective sol-gel ceramic membrane of Claim 1, wherein the porous substrate comprises silica, titania, zirconia, germania, alumina, graphite, silicon carbide, silicon nitride, boron nitride, borosilicate glass, lithium silicate, potassium silicate, tin oxide, iron oxide, carbon nanotubes, iron, or a combination thereof.~~

~~5. The nanoporous selective sol-gel ceramic membrane of Claim 1, wherein the porous support comprises a material selected from the group consisting of a~~

~~nonwoven fabric, a nonwoven mesh, a veil, a knit fabric, a woven fabric, a woven mesh, an open-cell foam, and a combination thereof.~~

~~6. The nanoporous selective sol-gel ceramic membrane of Claim 1, further comprising a compressible edging along at least a portion of an edge of the porous support formed by a polymeric material, wherein the polymeric material infiltrates the porous support by at least 1 um.~~

~~7. The nanoporous selective sol-gel ceramic membrane of Claim 6, wherein the compressible edging is along all edges of the porous support, defining a gasket.~~

~~8. The nanoporous selective sol-gel ceramic membrane of Claim 6, wherein the compressible edging covers 50% or less of a surface of the nanoporous selective sol-gel ceramic membrane.~~

~~9. The nanoporous selective sol-gel ceramic membrane of Claim 6, wherein the polymeric material of the compressible edging comprises an elastomeric polymer.~~

~~10. The nanoporous selective sol-gel ceramic membrane of Claim 1, wherein the nanoporous sol-gel ceramic composite is prepared by gelling a sol-gel precursor composition comprising one or more ceramic precursors.~~

~~11. The nanoporous selective sol-gel ceramic membrane of Claim 10, wherein the ceramic precursor is selected from the group consisting of silica, siloxane, silicate ester, silanol, silane, ormosil, titania, zirconia, germania, alumina, graphite, silicon carbide, silicon nitride, boron nitride, and combinations thereof.~~

~~12. The nanoporous selective sol-gel ceramic membrane of Claim 10, wherein the ceramic precursor comprises tetraalkyl orthosilicate.~~

~~13. The nanoporous selective sol-gel ceramic membrane of Claim 10, wherein the ceramic precursor comprises one or more organosilanes having the formula R^*_2-Si-~~

~~$(OR)_2$ or R* Si $(OR)_3$, wherein R*, independently at each occurrence, is an optionally substituted C1-C15 alkyl, optionally substituted C4-C20 heteroalkyl, optionally substituted aryl, or optionally substituted heteroaryl, and R, independently at each occurrence, is an optionally substituted C1-C6 alkyl.~~

~~14. The nanoporous selective sol-gel ceramic membrane of Claim 13, wherein the organosilane is C_6H_{13} Si $(OR)_3$.~~

~~15. The nanoporous selective sol-gel ceramic membrane of Claim 10 or Claim 13, wherein the ceramic precursor comprises colloidal ceramic particles.~~

~~16. The nanoporous selective sol-gel ceramic membrane of Claim 10, wherein the ceramic precursor comprises $Ti(OH)_x(OR)_y$, wherein R, independently at each occurrence, is a C1-C6 alkyl, x is an integer ranging from 0 to 4, and x is an integer ranging from 0 to 4, and the sum of x and y is 4.~~

~~17. The nanoporous selective sol-gel ceramic membrane of Claim 10, wherein the ceramic precursor comprises $Al(OR)_3$, wherein R, independently at each occurrence, is H or an optionally substituted C1-C6 alkyl.~~

~~18. The nanoporous selective sol-gel ceramic membrane of Claim 10, wherein the sol-gel precursor composition further comprises an additive selected from the group consisting of a catalyst, an ion-conducting polymer, electrically conductive particles, mechanical properties-improving materials, and a combination thereof.~~

~~19. The nanoporous selective sol-gel ceramic membrane of Claim 18, wherein the additive is present in an amount of 10 volume% or less of the sol-gel precursor composition.~~

~~20. The nanoporous selective sol-gel ceramic membrane of Claim 10, wherein the sol-gel precursor composition further comprises one or more organic solvents.~~

~~21. The nanoporous selective sol-gel ceramic membrane of Claim 10, wherein the organic solvent is a C1-C5 alcohol or a C6 arylene.~~

~~22. The nanoporous selective sol-gel ceramic membrane of Claim 1, wherein the nanoporous selective sol-gel ceramic membrane is of a type selected from the group consisting of a battery membrane, a fuel cell membrane, an electrodialysis membrane, an acid recovery membrane, a chloro-alkali membrane, a solvent extraction membrane, an electrodeposition membrane, and electrodeionization membrane, a nutrient recovery membrane, a food processing membrane, a reverse osmosis membrane, a gas separation membrane, and a bio-separation membrane.~~

~~23. The nanoporous selective sol-gel ceramic membrane of Claim 1, wherein the nanoporous selective sol-gel ceramic membrane is an ion-conducting membrane for a flow battery.~~

~~24. The nanoporous selective sol-gel ceramic membrane of Claim 1, wherein the nanoporous selective sol-gel ceramic membrane is an ion-conducting membrane for a fuel cell.~~

~~25. The nanoporous selective sol-gel ceramic membrane of Claim 1, wherein the nanoporous selective sol-gel ceramic membrane is an ion-conducting membrane for electrodialysis.~~

~~26. The nanoporous selective sol-gel ceramic membrane of Claim 1, wherein the nanoporous selective sol-gel ceramic membrane is an ion-conducting membrane for chloro-alkali processes.~~

~~27. The nanoporous selective sol-gel ceramic membrane of Claim 1, wherein the nanoporous selective sol-gel ceramic selective membrane has a mean pore size in a range of 0.5 nm to 2 nm as determined by fitting of its small angle x-ray scattering profile to a polydispersed fractal model.~~

28. The nanoporous selective sol-gel ceramic membrane of Claim 1, where in the nanoporous selective sol-gel ceramic membrane has an ionic area specific resistance (ASR) in the range of 0.01 Ohm*cm^2 to 10 Ohm*cm^2 when measured in 4 M H_2SO_4 or in the range of 0.1 Ohm*cm^2 to 100 Ohm*cm^2 when measured in 0.5 M NaCl.

29. A nanoporous selective sol-gel 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 sol-gel ceramic composite filling at least a portion of an active area of the porous support;

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

30. The nanoporous selective sol-gel ceramic membrane of Claim 29, wherein the mathematical model is a fractal aggregate model.

31. The nanoporous selective sol-gel ceramic membrane of Claim 30, 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.

32. The nanoporous selective sol-gel ceramic membrane of Claim 30, 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.

33. The nanoporous selective sol-gel ceramic membrane of Claim 32, 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_0 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.

34. The nanoporous selective sol-gel ceramic membrane of Claim 32, wherein the form factor, P(q), is a core-shell form factor of a sphere having a core and a shell, defined by the equation

$$P(q) = \frac{scale}{V_s}\left[3V_c(\rho_c - \rho_s)\frac{[\sin(qr_c) - qr_c\cos(qr_c)]}{(qr_c)^3} + 3V_s(\rho_s - \rho_{block})\frac{[\sin(qr_s) - qr\cos(qr_s)]}{(qr_s)^3}\right]^2 + bkg$$

wherein

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

V_e is a volume of the core,

V_s is a volume of the shell,

ρ_e is a scattering length density of the core,

ρ_s is a scattering length density of the shell,

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

r_e is a radius of the core,

r_s is a radius of the shell, and

bck is background scattering.

35. The nanoporous selective sol-gel ceramic membrane of Claim 34, wherein the surfaces of the nanoporous sol-gel ceramic are coated with a coating comprising an alkyl group.

36. The nanoporous selective sol-gel ceramic membrane of Claim 29, wherein a scattering intensity is fit to the mathematical model over a scattering vector, q, range of greater than an order of magnitude in units of $Å^{-1}$.

37. The nanoporous selective sol-gel ceramic membrane of Claim 36, 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 $Å^{-1}$.

38. The nanoporous selective sol-gel ceramic membrane according to any Claims 33 and 34, 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.

39. The nanoporous selective sol-gel ceramic membrane of Claim 33, wherein the fractal dimension, D_f, is constrained to a range of about 1 to about 3.

40. The nanoporous selective sol-gel ceramic membrane of Claim 33, 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.

41. The nanoporous selective sol-gel ceramic membrane of Claim 34, wherein

ρ_c is defined by a scattering length density of a material of the core,

ρ_s is defined by a scattering length density of a material of the shell, and

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

42. The nanoporous selective sol-gel ceramic membrane of Claim 30, wherein the fractal aggregate model is constrained to have pores of a radius less than 5nm.

43. The nanoporous selective sol-gel ceramic membrane of Claim 33, wherein the correlation length, ξ, is constrained to a value of greater than 1 nm.

44. The nanoporous selective sol-gel ceramic membrane according to any of Claims 33 and 34, wherein bck is allowed to vary during fitting.

45. The nanoporous selective sol-gel ceramic membrane of Claim 29, 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.

~~46. The nanoporous selective sol-gel ceramic membrane of Claim 29, wherein the mathematical model has a polydispersity ratio in a radius parameter.~~

~~47. The nanoporous selective sol-gel ceramic membrane of Claim 46, wherein the polydispersity ratio is constrained to less than 0.7.~~

~~48. The nanoporous selective sol-gel ceramic membrane of Claim 46, wherein the polydispersity ratio is from a Gaussian.~~

~~49. The nanoporous selective sol-gel ceramic membrane of Claim 46, wherein the polydispersity ratio is from a log-normal distribution.~~

~~50. The nanoporous selective sol-gel ceramic membrane of Claim 29, wherein the small-angle scattering spectra of the nanoporous sol-gel ceramic are measured after rinsing the nanoporous sol-gel ceramic to remove residual liquid and contaminants.~~

~~51. The nanoporous selective sol-gel ceramic membrane of Claim 29, wherein the small-angle scattering spectra of the nanoporous sol-gel ceramic are measured after drying the nanoporous sol-gel ceramic to remove solvent.~~

~~52. The nanoporous selective sol-gel ceramic membrane of Claim 29, wherein nanoporous sol-gel ceramic comprises greater than 20 mole % oxygen and greater than 10 mole % inorganic molecules.~~

~~53. The nanoporous selective sol-gel ceramic membrane of Claim 52, wherein the nanoporous sol-gel ceramic comprises a material selected from the group consisting of silica, alumina, titania, zirconia, germania, and combinations thereof.~~

~~54. The nanoporous selective sol-gel ceramic membrane of Claim 29, wherein the nanoporous sol-gel ceramic has a porosity volume fraction in a range of about 0.01 to about 0.7.~~

~~55. A selective membrane structure, comprising a plurality of individual selective membranes joined in a planar configuration.~~

~~56. The selective membrane structure of Claim 55, wherein the plurality of individual selective membranes are joined in a planar configuration by support members overlapping at least a portion of each of the plurality of individual selective membranes.~~

~~57. The selective membrane structure of Claim 55, wherein an active membrane surface area of the selective membrane structure including the plurality of individual selective membranes is greater than 50% of a total surface area of the selective membrane structure.~~

~~58. The selective membrane structure of Claim 55, wherein an active membrane surface area of the selective membrane structure including the plurality of individual selective membranes is in a range of about 50% to about 95%.~~

~~59. The selective membrane structure of Claim 55, wherein the support members comprise an ion exchange material.~~

~~60. The selective membrane structure of Claim 55, wherein the support members are disposed in a grid configuration to define a plurality of apertures into which the individual selective membranes are disposed.~~

~~61. The selective membrane structure of Claim 55, wherein the individual selective membranes comprise:~~

~~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 active area of the porous support.~~

~~62. The selective membrane structure of Claim 61, wherein the nanoporous composite comprises a plurality of nanopores of 5 nm or smaller in radius with a polydispersity index of 0.5 or lower.~~

~~63. The selective membrane structure of Claim 61, wherein the nanoporous sol-gel ceramic has a fractal nanoporous structure as determined by fitting small angle scattering spectra of the nanoporous sol-gel ceramic to a mathematical model.~~

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.