

CAPACITY BOOSTERS FOR VANADIUM-BASED ELECTROLYTES

FIELD OF INVENTION

5 The current invention relates to a composite material suitable for boosting the capacity of a $\text{VO}^{2+}/\text{VO}_2^+$ electrolytic flow cell battery, and a $\text{VO}^{2+}/\text{VO}_2^+$ flow cell battery comprising a capacity boosting material that has a redox potential that is about the same as the redox potential of $\text{VO}^{2+}/\text{VO}_2^+$, as measured relative to a standard hydrogen electrode.

10 BACKGROUND

The listing or discussion of a prior-published document in this specification should not necessarily be taken as an acknowledgement that the document is part of the state of the art or is common general knowledge.

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Prior to this invention, Cheng and coworkers used vanadium-based Prussian blue analogue material to enhance the capacity of $\text{VO}^{2+}/\text{VO}_2^+$ electrolyte (Cheng, Y. et al., *ACS Energy Letters*, **2019**, 4, 3028-3035). As opposed to the mentioned prior art, this invention discloses a series of vanadium-free capacity boosting materials for the $\text{VO}^{2+}/\text{VO}_2^+$ electrolyte.

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The series of materials considerably enhanced the capacity of the $\text{VO}^{2+}/\text{VO}_2^+$ electrolyte for flow battery application. One important application is to use as the catholyte system for all-vanadium flow battery. With all-vanadium flow battery as an example, the presence of capacity boosting materials in the catholyte tank promotes catholyte capacity. The capacity
25 boosting materials disclosed could considerably enhance the capacity of the battery without increasing the concentration of vanadium and sulfuric acid, therefore reduces the consumption of vanadium species and consequently the cost spent on electrolytes. In addition, without sacrificing the capacity, thermal stability of the electrolyte at elevated temperature is also enhanced at reduced $\text{VO}^{2+}/\text{VO}_2^+$ concentration, and this further reduces
30 the processing costs incurred from cooling. Also, the use of easily synthesized and environmentally friendly capacity boosters reduces the processing costs and the environmental hazards.

SUMMARY

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Aspects and embodiments of the current invention will now be described by reference to the following numbered clauses.

1. A composite material suitable for boosting the capacity of a $\text{VO}^{2+}/\text{VO}_2^+$ electrolytic flow cell battery, the composite material comprising:

a capacity boosting material for a $\text{VO}^{2+}/\text{VO}_2^+$ flow cell;

5 a carbon black; and

a binder,

wherein:

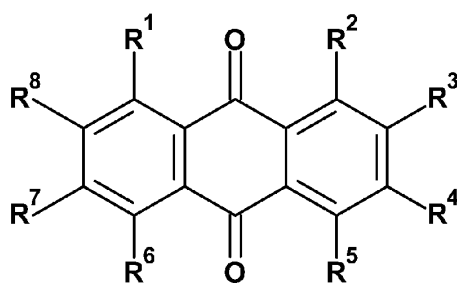
the capacity boosting material for a $\text{VO}^{2+}/\text{VO}_2^+$ flow cell is a material that is insoluble or is poorly soluble in an electrolyte suitable for use in a $\text{VO}^{2+}/\text{VO}_2^+$ flow cell; and

10 the capacity boosting material for a $\text{VO}^{2+}/\text{VO}_2^+$ flow cell is a material that has a redox potential that is about the same as the redox potential of $\text{VO}^{2+}/\text{VO}_2^+$, as measured relative to a standard hydrogen electrode.

2. The composite material according to Clause 1, wherein the capacity boosting material has a redox potential that is within 5% of the redox potential of $\text{VO}^{2+}/\text{VO}_2^+$, as measured relative to a standard hydrogen electrode.

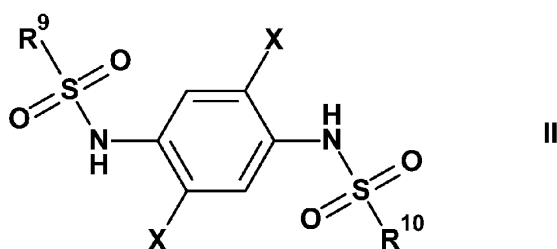
3. The composite material according to Clause 2, wherein the capacity boosting material has a redox potential that is identical to the redox potential of $\text{VO}^{2+}/\text{VO}_2^+$, as measured relative to a standard hydrogen electrode.

4. The composite material according to any one of the preceding clauses, wherein the capacity boosting material has the formula I or the formula II:



I

; or



where:

R¹ to R⁸ are each independently selected from H, C₁ to C₁₀ alkyl or OH, provided that at two
 5 of R¹ to R⁸ are OH;

R⁹ and R¹⁰ are each independently selected from a C₁ to C₂₀ alkyl group, an aryl group or a
 heteroaryl group, where each of the aryl and heteroaryl groups are unsubstituted or
 substituted by one or more groups selected from methyl, ethyl, methoxy, nitro and halo; and
 X is independently selected from Cl, Br, F, or

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the capacity boosting material is a polymeric material derived from the compound of formula
 II.

5. The composite material according to Clause 4, wherein the capacity boosting
 15 material is selected from one or more of the group consisting of:

- (a) 2,5-dichloro-1,4-phenylene bis((propylsulfonyl)amide);
- (b) 1,4-dihydroxyanthraquinone;
- (c) 1,2-dihydroxyanthraquinone;
- (d) 1,5-dihydroxyanthraquinone; and
- 20 (e) 1,8-dihydroxyanthraquinone.

6. The composite material according to Clause 5, wherein the capacity boosting
 material is selected from one or more of the group consisting of:

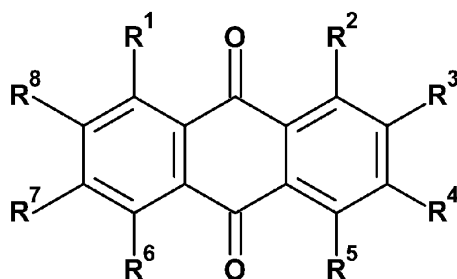
- (a) 2,5-dichloro-1,4-phenylene bis((propylsulfonyl)amide); and
- 25 (b) 1,4-dihydroxyanthraquinone.

7. The composite material according to any one of the preceding clauses, wherein the
 composite material is insoluble or is poorly soluble in an electrolyte suitable for use in a
 VO²⁺/VO₂⁺ electrolytic flow cell.

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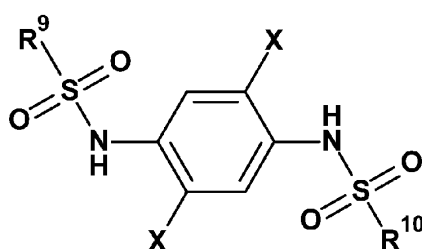
8. A $\text{VO}^{2+}/\text{VO}_2^+$ flow cell battery comprising a capacity boosting material that has a redox potential that is about the same as the redox potential of $\text{VO}^{2+}/\text{VO}_2^+$, as measured relative to a standard hydrogen electrode.
- 5 9. The flow cell battery according to Clause 8, wherein the flow cell comprises:
a catholyte tank;
an anolyte tank; and
a redox flow cell comprising a cathode compartment, having a cathode electrode,
and an anode compartment, having an anode electrode, separated by an ion selective
10 membrane, where the cathode electrode and anode electrode are connectable to an energy
harvesting or utilising device, where
the catholyte tank comprises the capacity boosting material as defined in Clause 8,
 $\text{VO}^{2+}/\text{VO}_2^+$, water and an acidic electrolyte support, and the catholyte tank is fluidly
connected to the cathode compartment of the redox flow cell; and
15 the anolyte tank comprises a different redox couple with a lower redox potential than
 $\text{VO}^{2+}/\text{VO}_2^+$, water and an acidic electrolyte support, and the anolyte tank is fluidly connected
to the anode compartment of the redox flow cell.
10. The flow cell battery according to Clause 8 or Clause 9, wherein one or more of the
20 following apply:
the capacity boosting material for a $\text{VO}^{2+}/\text{VO}_2^+$ flow cell is a material that is insoluble
or is poorly soluble in an electrolyte suitable for use in a $\text{VO}^{2+}/\text{VO}_2^+$ flow cell; and
the capacity boosting material has a redox potential that is within 5% of the redox
potential of $\text{VO}^{2+}/\text{VO}_2^+$, as measured relative to a standard hydrogen electrode (e.g. the
25 capacity boosting material has a redox potential that is identical to the redox potential of
 $\text{VO}^{2+}/\text{VO}_2^+$, as measured relative to a standard hydrogen electrode).
11. The flow cell battery according to any one of Clause 8 to 10, wherein the capacity
boosting material has the formula I or the formula II:

5



I

; or



II

5 where:

R¹ to R⁸ are each independently selected from H, C₁ to C₁₀ alkyl or OH, provided that at two of R¹ to R⁸ are OH;

R⁹ and R¹⁰ are each independently selected from a C₁ to C₂₀ alkyl group an aryl group or a heteroaryl group, where each of the aryl and heteroaryl groups are unsubstituted or substituted by one or more groups selected from methyl, ethyl, methoxy, nitro and halo; and
 10 X is independently selected from Cl, Br, F, or

the capacity boosting material is a polymeric material derived from the compound of formula II.

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12. The flow cell battery according to Clause 11, wherein the capacity boosting material is selected from one or more of the group consisting of:

- (a) 2,5-dichloro-1,4-phenylene bis((propylsulfonyl)amide);
- (b) 1,4-dihydroxyanthraquinone;
- 20 (c) 1,2-dihydroxyanthraquinone;
- (d) 1,5-dihydroxyanthraquinone; and
- (e) 1,8-dihydroxyanthraquinone, optionally wherein the capacity boosting material is selected from one or more of the group consisting of:

- (a) 2,5-dichloro-1,4-phenylene bis((propylsulfonyl)amide); and
- (b) 1,4-dihydroxyanthraquinone.

13. The flow cell battery according to any one of Clauses 8 to 12, wherein the capacity
5 boosting material is provided in a composite material as described in any one of Clauses 1 to 7.

14. The flow cell battery according to any one of Clause 8 to 13, wherein the different
redox couple with a lower redox potential than $\text{VO}^{2+}/\text{VO}_2^+$ is selected from one or more of the
10 group consisting of $\text{V}^{2+}/\text{V}^{3+}$, $\text{TiO}^{2+}/\text{Ti}^{3+}$, H_2/H^+ , and $\text{Cr}^{2+}/\text{Cr}^{3+}$.

15. A method of using a capacity boosting material suitable for boosting the capacity of
a $\text{VO}^{2+}/\text{VO}_2^+$ flow cell battery, the method comprising the steps of:

- (a) providing a $\text{VO}^{2+}/\text{VO}_2^+$ flow cell battery, the battery comprising
15 a catholyte tank;
an anolyte tank; and
a redox flow cell comprising a cathode compartment, having a cathode electrode,
and an anode compartment, having an anode electrode, separated by an ion selective
membrane, where the cathode electrode and anode electrode are connectable to an energy
20 harvesting or utilising device, where
the catholyte tank comprises:
a capacity boosting material that has a redox potential that is about the same
as the redox potential of $\text{VO}^{2+}/\text{VO}_2^+$, as measured relative to a standard hydrogen
electrode;
25 $\text{VO}^{2+}/\text{VO}_2^+$; and
a catholyte comprising water and an acidic electrolyte support, and the
catholyte tank is fluidly connected to the cathode compartment of the redox flow cell;
and
the anolyte tank comprises a different redox couple with a lower redox potential than
30 $\text{VO}^{2+}/\text{VO}_2^+$, water and an acidic electrolyte support, and the anolyte tank is fluidly connected
to the anode compartment of the redox flow cell; and
(b) operating the battery to generate electricity through cycling the catholyte and anolyte
from the catholyte and anolyte tanks into the cathode and anode compartments, respectively,
and returning the catholyte and anolyte to the catholyte and anolyte tanks, respectively in a
35 continuous sequence until the battery is discharged,
wherein, in a charged state, VO_2^+ is the predominant form of the $\text{VO}_2^+/\text{VO}_2^+$ and the
capacity boost material is predominantly in a reduced state, and in a fully discharged state

VO^{2+} is the predominant form of the $\text{VO}_2^+/\text{VO}_2^+$ and the capacity boost material is predominantly in an oxidised state.

16. A method of charging a $\text{VO}^{2+}/\text{VO}_2^+$ flow cell battery as described in Clause 15
 5 wherein the method comprises applying electricity to the flow cell and cycling the catholyte and anolyte from the catholyte and anolyte tanks into the cathode and anode compartments, respectively, and returning the catholyte and anolyte to the catholyte and anolyte tanks, respectively in a continuous sequence until the battery is charged, wherein in a fully discharged state VO^{2+} is the predominant form of the $\text{VO}_2^+/\text{VO}_2^+$ and the capacity boost
 10 material is predominantly in an oxidised state and in a charged state, VO_2^+ is the predominant form of the $\text{VO}_2^+/\text{VO}_2^+$ and the capacity boost material is predominantly in a reduced state.

17. The method according to Clause 15 or Clause 16, wherein the different redox couple
 15 with a lower redox potential than $\text{VO}^{2+}/\text{VO}_2^+$ is selected from one or more of the group consisting of $\text{V}^{2+}/\text{V}^{3+}$, $\text{TiO}^{2+}/\text{Ti}^{3+}$, H_2/H^+ , and $\text{Cr}^{2+}/\text{Cr}^{3+}$.

BRIEF DESCRIPTION OF DRAWINGS

20 FIG. 1 depicts (a) a schematic illustration of the system incorporating a solid capacity booster in the $\text{VO}^{2+}/\text{VO}_2^+$ electrolyte tank; and (b) principle of $\text{VO}^{2+}/\text{VO}_2^+$ -mediated chemical and electrochemical reactions during discharge of the battery system.

FIG. 2 depicts (a) cyclic voltammetry (CV) curves of 1,4-dihydroxyanthraquinone (1,4-DHAQ) and that of VOSO_4 in 0.5 M sulfuric acid solution; and (b) CV curves of 2,5-dichloro-
 25 1,4-phenylene bis((propylsulfonyl)amide) (Propyl-HDC) and that of VOSO_4 in 0.5 M sulfuric acid solution.

FIG. 3 depicts (a) molecular structure of anthraquinone derivative, for which each R is
 30 independently H, alkyl, or OH group; and (b) molecular structure of 2,5-dichloro-1,4-phenylene bis((alkyl (or) aryl (or) heteroaryl sulfonyl)amide), for which each R is independently an alkyl group $\text{C}_n\text{H}_{2n+1}$ ($n=1-20$) or aryl (unsubstituted and substituted) or heteroaryl (unsubstituted and substituted) groups.

35 FIG. 4 depicts (a) the battery capacity and coulombic efficiency before and after addition of Propyl-HDC capacity booster at different number of cycles of a symmetric cell; and (b) the voltage profiles in different numbers of cycles; the current density is $10 \text{ mA}/\text{cm}^2$.

DESCRIPTION

It has been surprisingly found that certain materials can act as capacity boosting materials (whether in a free form or in a composite material) to boost the capacity of a $\text{VO}^{2+}/\text{VO}_2^+$ electrolytic flow cell battery. As demonstrated herein, the presence of these vanadium-free capacity boosting materials in the catholyte tank of the $\text{VO}^{2+}/\text{VO}_2^+$ flow cell battery promotes the catholyte capacity without increasing the vanadium concentration, thereby reducing the consumption of vanadium and the cost of operation. In addition, these capacity boosters are considered to be environmentally friendly.

As such, in a first aspect of the invention, there is provided a composite material suitable for boosting the capacity of a $\text{VO}^{2+}/\text{VO}_2^+$ electrolytic flow cell battery, the composite material comprising:

- a capacity boosting material for a $\text{VO}^{2+}/\text{VO}_2^+$ flow cell;
- a carbon black; and
- a binder,

wherein:

- the capacity boosting material for a $\text{VO}^{2+}/\text{VO}_2^+$ flow cell is a material that is insoluble or is poorly soluble in an electrolyte suitable for use in a $\text{VO}^{2+}/\text{VO}_2^+$ flow cell; and
- the capacity boosting material for a $\text{VO}^{2+}/\text{VO}_2^+$ flow cell is a material that has a redox potential that is about the same as the redox potential of $\text{VO}^{2+}/\text{VO}_2^+$, as measured relative to a standard hydrogen electrode.

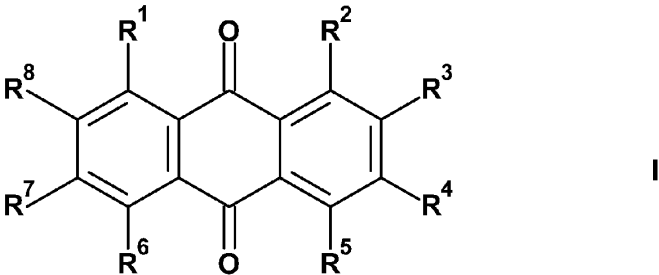
The word "comprising" refers herein may be interpreted as requiring the features mentioned, but not limiting the presence of other features. Alternatively, the word "comprising" may also relate to the situation where only the components/features listed are intended to be present (e.g. the word "comprising" may be replaced by the phrases "consists of" or "consists essentially of"). It is explicitly contemplated that both the broader and narrower interpretations can be applied to all aspects and embodiments of the present invention. In other words, the word "comprising" and synonyms thereof may be replaced by the phrase "consisting of" or the phrase "consists essentially of" or synonyms thereof and *vice versa*.

The phrase, "consists essentially of" and its pseudonyms may be interpreted herein to refer to a material where minor impurities may be present. For example, the material may be greater than or equal to 90% pure, such as greater than 95% pure, such as greater than

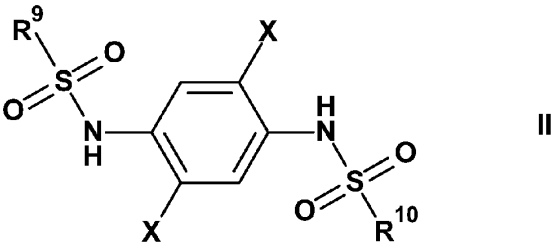
97% pure, such as greater than 99% pure, such as greater than 99.9% pure, such as greater than 99.99% pure, such as greater than 99.999% pure, such as 100% pure.

As used herein, the singular forms “a,” “an,” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a composition” includes mixtures of two or more such compositions, and the like.

The capacity boosting material for a $\text{VO}^{2+}/\text{VO}_2^+$ flow cell is a material that has a redox potential that is about the same as the redox potential of $\text{VO}^{2+}/\text{VO}_2^+$, as measured relative to a standard hydrogen electrode. This may be a redox potential within 10%, such as within 7%, such as within 6% of the redox potential of $\text{VO}^{2+}/\text{VO}_2^+$, as measured relative to a standard hydrogen electrode. In particular embodiments of the invention that may be mentioned herein, the capacity boosting material may have a redox potential that is within 5% of the redox potential of $\text{VO}^{2+}/\text{VO}_2^+$, as measured relative to a standard hydrogen electrode. In particular embodiments of the invention the capacity boosting material may have a redox potential that is identical to the redox potential of $\text{VO}^{2+}/\text{VO}_2^+$, as measured relative to a standard hydrogen electrode. In yet more particular embodiments of the invention, the capacity boosting material may have the formula I or the formula II:



; or



where:

R¹ to R⁸ are each independently selected from H, C₁ to C₁₀ alkyl or OH, provided that at two of R¹ to R⁸ are OH;

R⁹ and R¹⁰ are each independently selected from a C₁ to C₂₀ alkyl group an aryl group or a
5 heteroaryl group, where each of the aryl and heteroaryl groups are unsubstituted or substituted by one or more groups selected from methyl, ethyl, methoxy, nitro and halo; and
X is independently selected from Cl, Br, F, or

the capacity boosting material may be a polymeric material derived from the compound of
10 formula II.

Unless otherwise stated, the term "alkyl" refers to an unbranched or branched, acyclic or cyclic, saturated or unsaturated (so forming, for example, an alkenyl or alkynyl) hydrocarbyl radical, which may be substituted or unsubstituted (with, for example, one or more halo
15 atoms). Where the term "alkyl" refers to an acyclic group, it is preferably C₁₋₂₀ alkyl and, more preferably, C₁₋₈ alkyl (such as methyl, ethyl, propyl, (e.g. n-propyl or isopropyl), butyl (e.g. n-butyl or isobutyl), pentyl (e.g. unbranched or branched), hexyl (e.g. unbranched or branched)). Where the term "alkyl" is a cyclic group (which may be where the group "cycloalkyl" is specified), it is preferably C₃₋₁₂ cycloalkyl and, more preferably, C₅₋₁₀ (e.g. C₅₋₇)
20 cycloalkyl.

Unless otherwise stated, the term "aryl" when used herein includes C₆₋₁₄ (such as C₆₋₁₀) aryl groups. Such groups may be monocyclic, bicyclic or tricyclic and have between 6 and 14 ring carbon atoms, in which at least one ring is aromatic. The point of attachment of aryl
25 groups may be *via* any atom of the ring system. However, when aryl groups are bicyclic or tricyclic, they are linked to the rest of the molecule *via* an aromatic ring. C₆₋₁₄ aryl groups include phenyl, naphthyl and the like, such as 1,2,3,4-tetrahydronaphthyl, indanyl, indenyl and fluorenyl. Embodiments of the invention that may be mentioned include those in which aryl is phenyl.

30 The term "heteroaryl" when used herein refers to an aromatic group containing one or more heteroatom(s) (e.g. one to four heteroatoms) preferably selected from N, O and S (so forming, for example, a mono-, bi-, or tricyclic heteroaromatic group). Heteroaryl groups include those which have between 5 and 14 (e.g. 10) members and may be monocyclic,
35 bicyclic or tricyclic, provided that at least one of the rings is aromatic. However, when heteroaryl groups are bicyclic or tricyclic, they are linked to the rest of the molecule *via* an aromatic ring. Heterocyclic groups that may be mentioned include benzothiadiazolyl

(including 2,1,3-benzothiadiazolyl), isothiochromanyl and, more preferably, acridinyl, benzimidazolyl, benzodioxanyl, benzodioxepinyl, benzodioxolyl (including 1,3-benzodioxolyl), benzofuranyl, benzofurazanyl, benzothiazolyl, benzoxadiazolyl (including 2,1,3-benzoxadiazolyl), benzoxazinyl (including 3,4-dihydro-2H-1,4-benzoxazinyl), benzoxazolyl, 5 benzomorpholinyl, benzoselenadiazolyl (including 2,1,3-benzoselenadiazolyl), benzothienyl, carbazolyl, chromanyl, cinnolinyl, furanyl, imidazolyl, imidazo[1,2-a]pyridyl, indazolyl, indolinyl, indolyl, isobenzofuranyl, isochromanyl, isoindolinyl, isoindolyl, isoquinolinyl, isothiazolyl, isoxazolyl, naphthyridinyl (including 1,6-naphthyridinyl or, preferably, 1,5-naphthyridinyl and 1,8-naphthyridinyl), oxadiazolyl (including 1,2,3-oxadiazolyl, 1,2,4-oxadiazolyl and 1,3,4-oxadiazolyl), oxazolyl, phenazinyl, phenothiazinyl, phthalazinyl, 10 pteridinyl, purinyl, pyranyl, pyrazinyl, pyrazolyl, pyridazinyl, pyridyl, pyrimidinyl, pyrrolyl, quinazolinyl, quinolinyl, quinoliziny, quinoxalinyl, tetrahydroisoquinolinyl (including 1,2,3,4-tetrahydroisoquinolinyl and 5,6,7,8-tetrahydroisoquinolinyl), tetrahydroquinolinyl (including 1,2,3,4-tetrahydroquinolinyl and 5,6,7,8-tetrahydroquinolinyl), tetrazolyl, thiadiazolyl 15 (including 1,2,3-thiadiazolyl, 1,2,4-thiadiazolyl and 1,3,4-thiadiazolyl), thiazolyl, thiochromanyl, thiophenetyl, thienyl, triazolyl (including 1,2,3-triazolyl, 1,2,4-triazolyl and 1,3,4-triazolyl) and the like. Substituents on heteroaryl groups may, where appropriate, be located on any atom in the ring system including a heteroatom. The point of attachment of heteroaryl groups may be via any atom in the ring system including (where appropriate) a 20 heteroatom (such as a nitrogen atom), or an atom on any fused carbocyclic ring that may be present as part of the ring system. Heteroaryl groups may also be in the N- or S-oxidised form. Particularly preferred heteroaryl groups include pyridyl, pyrrolyl, quinolinyl, furanyl, thienyl, oxadiazolyl, thiadiazolyl, thiazolyl, oxazolyl, pyrazolyl, triazolyl, tetrazolyl, isoxazolyl, isothiazolyl, imidazolyl, pyrimidinyl, indolyl, pyrazinyl, indazolyl, pyrimidinyl, thiophenetyl, 25 thiophenyl, pyranyl, carbazolyl, acridinyl, quinolinyl, benzoimidazolyl, benzthiazolyl, purinyl, cinnolinyl and pteridinyl. Particularly preferred heteroaryl groups include monocyclic heteroaryl groups.

As noted above, the capacity boosting material is a polymeric material derived from the 30 compound of formula II. The polymeric material may be derived from the compound of formula II through the positioning of polymerisable groups in the R⁹ and/or R¹⁰ groups. For example, R⁹ and/or R¹⁰ may contain a vinyl group, thereby allowing polymerisation to occur.

In particular embodiments of the invention that may be mentioned herein, the capacity 35 boosting material may be selected from one or more of the group consisting of:

- (a) 2,5-dichloro-1,4-phenylene bis((propylsulfonyl)amide);
- (b) 1,4-dihydroxyanthraquinone;

- (c) 1,2-dihydroxyanthraquinone;
- (d) 1,5-dihydroxyanthraquinone; and
- (e) 1,8-dihydroxyanthraquinone.

- 5 In yet more particular embodiments of the invention, the capacity boosting material may be selected from one or more of the group consisting of:
- (a) 2,5-dichloro-1,4-phenylene bis((propylsulfonyl)amide); and
 - (b) 1,4-dihydroxyanthraquinone.
- 10 As noted herein, the composite material may be insoluble or is poorly soluble in an electrolyte suitable for use in a $\text{VO}^{2+}/\text{VO}_2^+$ electrolytic flow cell. For example, the composite material may have a maximum dissolved concentration in the electrolyte suitable for use in a $\text{VO}^{2+}/\text{VO}_2^+$ electrolytic flow cell of 50 mM as measured at room temperature after at least one hour of exposure to the electrolyte. In certain embodiments, the composite material may
- 15 have a maximum dissolved concentration in the electrolyte suitable for use in a $\text{VO}^{2+}/\text{VO}_2^+$ electrolytic flow cell of 40 mM, such as 30 mM, such as 20 mM, such as about 10 mM, as measured at room temperature after at least one hour of exposure to the electrolyte.

Any suitable electrolyte may be used herein. For example, the electrolyte may comprise

20 water and a suitable acid (e.g. sulphuric acid).

The capacity boosting material (whether in a free form or in a composite material) may be particularly suited for application as part of the catholyte system for a vanadium flow battery (e.g. as part of an all-vanadium flow battery). The capacity boosting materials disclosed

25 herein may considerably enhance the capacity of the battery without the need to increase the concentration of vanadium and sulfuric acid. As a result, material costs can be greatly reduced and the thermal stability of the battery may be enhanced, which may help to further reduce costs incurred from cooling the battery. In addition, the capacity booster may be considered to be environmentally friendly.

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In a further aspect of the invention, there is provided a $\text{VO}^{2+}/\text{VO}_2^+$ flow cell battery comprising a capacity boosting material that has a redox potential that is about the same as the redox potential of $\text{VO}^{2+}/\text{VO}_2^+$, as measured relative to a standard hydrogen electrode. More particularly, the flow cell battery may be one that comprises:

- 35 a catholyte tank;
an anolyte tank; and

a redox flow cell comprising a cathode compartment, having a cathode electrode, and an anode compartment, having an anode electrode, separated by an ion selective membrane, where the cathode electrode and anode electrode are connectable to an energy harvesting or utilising device, where

5 the catholyte tank comprises the capacity boosting material as defined herein, $\text{VO}^{2+}/\text{VO}_2^+$, water and an acidic electrolyte support, and the catholyte tank is fluidly connected to the cathode compartment of the redox flow cell; and

the anolyte tank comprises a different redox couple with a lower redox potential than $\text{VO}^{2+}/\text{VO}_2^+$, water and an acidic electrolyte support, and the anolyte tank is fluidly connected
10 to the anode compartment of the redox flow cell.

The acidic electrolyte support used in the catholyte and anolyte may comprise water and a suitable acid (e.g. sulphuric acid). The acid may be present in any suitable concentration, such as from 0.1 to 4 M, such as from 0.3 to 1 M, such as about 0.6 M.

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In embodiments of the flow cell battery, the capacity boosting material may be as described hereinbefore. As details of the capacity boosting material for a $\text{VO}^{2+}/\text{VO}_2^+$ flow cell have already been described above, they are omitted here for brevity.

20 The capacity boosting material may be used in a "free" state – that is, as the material *per se*. Alternatively or additionally, the capacity boosting material may provided in a composite material as described in the first aspect of the invention and any technically sensible combination of its embodiments.

25 Any suitable different redox couple with a lower redox potential than $\text{VO}^{2+}/\text{VO}_2^+$ may be used in embodiments of the invention. Examples of suitable redox couples include, but are not limited to $\text{V}^{2+}/\text{V}^{3+}$, $\text{TiO}^{2+}/\text{Ti}^{3+}$, H_2/H^+ , $\text{Cr}^{2+}/\text{Cr}^{3+}$, and combinations thereof.

Both electrodes in the redox-mediated metal-air fuel cell system, i.e., the cathode and the
30 anode, can be a carbon, a metal, or a combination thereof. Preferably, these two electrodes have high surface area, with or without one or more catalysts, to facilitate the charge collection process. They can be made of a carbon, a metal, or a combination thereof. Examples of an electrode can be found in Skyllas-Kazacos, *et al.*, *Journal of The Electrochemical Society*, **2011**, 158, R55-79, and Weber, *et al.*, *Journal of Applied
35 Electrochemistry*, **2011**, 41, 1137-64. The discussion above in relation to the cathode may be particularly true for a cathode electrode situated in a cathode compartment that has an

inlet and outlet suitable for the bubbling of a gas through the cathode compartment, such a compartment may be suitable for the use of a liquid catholyte.

The ion-selective membrane when mentioned herein may be an electro-active charge
5 balancing ion conducting membrane (e.g. a proton, potassium, lithium or sodium ion
conducting membrane). The ion-selective membrane prevents cross-diffusion of the redox
mediator and allows for movement of electro-active charge balancing ions (e.g. protons,
potassium, lithium ions, sodium ions, magnesium ions, aluminium ions, copper ions, or a
10 combination thereof). For example, the ion-selective membrane may be a Nafion™
membrane, a lithium phosphorus oxynitride glass, a lithium thiophosphate glass, sodium
phosphorus oxynitride glass, a sodium thiophosphate glass, a NASICON-type lithium
conducting glass ceramic, a NASICON-type sodium conducting glass ceramic, a Garnet-
type lithium or sodium conducting glass ceramic, a ceramic nanofiltration membrane, a
lithium or sodium ion-exchange membrane, or suitable combinations thereof.

15 In a further aspect of the invention, there is provided a method of using a capacity boosting
material suitable for boosting the capacity of a $\text{VO}^{2+}/\text{VO}_2^+$ flow cell battery, the method
comprising the steps of:

- (a) providing a $\text{VO}^{2+}/\text{VO}_2^+$ flow cell battery, the battery comprising
20 a catholyte tank;
an anolyte tank; and
a redox flow cell comprising a cathode compartment, having a cathode electrode,
and an anode compartment, having an anode electrode, separated by an ion selective
membrane, where the cathode electrode and anode electrode are connectable to an energy
25 harvesting or utilising device, where
the catholyte tank comprises:
a capacity boosting material that has a redox potential that is about the same
as the redox potential of $\text{VO}^{2+}/\text{VO}_2^+$, as measured relative to a standard hydrogen
electrode;
30 $\text{VO}^{2+}/\text{VO}_2^+$; and
a catholyte comprising water and an acidic electrolyte support, and the
catholyte tank is fluidly connected to the cathode compartment of the redox flow cell;
and
the anolyte tank comprises a different redox couple with a lower redox potential than
35 $\text{VO}^{2+}/\text{VO}_2^+$, water and an acidic electrolyte support, and the anolyte tank is fluidly connected
to the anode compartment of the redox flow cell; and

- (b) operating the battery to generate electricity through cycling the catholyte and anolyte from the catholyte and anolyte tanks into the cathode and anode compartments, respectively, and returning the catholyte and anolyte to the catholyte and anolyte tanks, respectively in a continuous sequence until the battery is discharged,
- 5 wherein, in a charged state, VO_2^+ is the predominant form of the $\text{VO}_2^+/\text{VO}_2^+$ and the capacity boost material is predominantly in a reduced state, and in a fully discharged state VO^{2+} is the predominant form of the $\text{VO}_2^+/\text{VO}_2^+$ and the capacity boost material is predominantly in an oxidised state.
- 10 In a charging cycle, the method may comprise applying electricity to the flow cell and cycling the catholyte and anolyte from the catholyte and anolyte tanks into the cathode and anode compartments, respectively, and returning the catholyte and anolyte to the catholyte and anolyte tanks, respectively in a continuous sequence until the battery is charged, wherein in a fully discharged state VO^{2+} is the predominant form of the $\text{VO}_2^+/\text{VO}_2^+$ and the capacity
- 15 boost material is predominantly in an oxidised state and in a charged state, VO_2^+ is the predominant form of the $\text{VO}_2^+/\text{VO}_2^+$ and the capacity boost material is predominantly in a reduced state.

As details of the capacity boosting material (in a free or composite material form) and the different redox couple are provided hereinbefore, they are omitted in discussion of this aspect of the invention, as the same materials mentioned hereinbefore may be used.

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Advantages associated with the aspects and embodiments of the invention include, but are not limited to:

- 25
- enhancing the capacity of a $\text{VO}^{2+}/\text{VO}_2^+$ battery system through the inclusion of a capacity booster material as described herein;
 - avoiding the need to increase vanadium concentration through the use of the capacity booster material disclosed herein, which may help to boost battery stability and other aspects of performance of the battery, with potential costs savings through
- 30
- making use of an easily synthesised and environmentally friendly capacity booster material that may help to reduce processing costs and environmental hazards associated with vanadium batteries.

35 All of the features disclosed in this specification may be combined in any combination. Each feature disclosed in this specification may be replaced by an alternative feature serving the

same, equivalent, or similar purpose. Thus, unless expressly stated otherwise, each feature disclosed is only an example of a generic series of equivalent or similar features.

From the above description, one skilled in the art can easily ascertain the essential characteristics of the present invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions. Thus, other embodiments are also within the claims.

Hereinafter, embodiments of the invention are illustrated in more detail with reference to the following examples. However, the present disclosure is not limited thereto. Furthermore, what is not described in this disclosure may be sufficiently understood by those who have knowledge in this field and will not be illustrated herein.

The following Examples illustrate the invention.

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EXAMPLES

Example 1: $\text{VO}^{2+}/\text{VO}_2^+$ -mediated Capacity Boosting Process

FIG. 1a shows a schematic illustration of the system incorporating the solid capacity booster in the $\text{VO}^{2+}/\text{VO}_2^+$ electrolyte tank. FIG. 1b shows the principle of $\text{VO}^{2+}/\text{VO}_2^+$ -mediated chemical and electrochemical reactions during the discharge of a battery system.

Working Principle of the $\text{VO}^{2+}/\text{VO}_2^+$ -mediated Capacity Boosting Process

The working principle of the $\text{VO}^{2+}/\text{VO}_2^+$ -mediated capacity boosting process is based on a redox-targeting reaction between the $\text{VO}^{2+}/\text{VO}_2^+$ redox mediator and solid capacity boosting material of identical redox potentials.

Charge Process

Taking the charge process as an example, during which VO^{2+} is oxidized to VO_2^+ electrochemically on the electrode, the potential of $\text{VO}^{2+}/\text{VO}_2^+$ increases to be higher than the solid capacity booster when VO_2^+ is predominant in the electrolyte solution. Thus, VO_2^+ is able to oxidize the solid material and itself is reduced to VO^{2+} in the storage tank. VO^{2+} is oxidized again at the electrode when it flows into the electrode compartment and starts the next round of reactions.

Discharge Process

Similarly, during the discharge process, VO^{2+} is predominant and the potential of $\text{VO}^{2+}/\text{VO}_2^+$ becomes lower than the solid materials. Thus, it can reduce the oxidized solid material. Through the multi-fold redox-targeting reactions, reversible charge and discharge of solid capacity boosting material in the storage tank can be achieved.

Results and Discussions

The Nernstian potential difference induced by the activity changes of $\text{VO}^{2+}/\text{VO}_2^+$ upon charging/discharging would make the reactions energetically favourable for the reduced capacity booster to be chemically oxidized by VO_2^+ during the charge process and reversely for the oxidized capacity booster to be chemically reduced by VO^{2+} during the discharge process. Compared to the sole $\text{VO}^{2+}/\text{VO}_2^+$ electrolyte, this method can enhance the capacity due to the incorporation of solid material with a higher capacity for charge storage. The energy density of the whole system is also enhanced.

Example 2: Capacity Boosters for the $\text{VO}^{2+}/\text{VO}_2^+$ Electrolyte

Stable Capacity Boosters with Matching Potentials with the $\text{VO}^{2+}/\text{VO}_2^+$ Electrolyte

Stable capacity booster (solid materials) with potentials matched with $\text{VO}^{2+}/\text{VO}_2^+$ could be used. Here 1,4-dihydroxyanthraquinone (1,4-DHAQ) and 2,5-dichloro-1,4-phenylene bis((propylsulfonyl)amide) (Propyl-HDC) are shown as two examples. The redox potential of 1,4-DHAQ and Propyl-HDC was measured in 0.5 M sulfuric acid by cyclic voltammetry (CV) method.

Other anthraquinone derivatives (i.e., 1,2-DHAQ, 1,5-DHAQ, 1,8-DHAQ) were also tested. The structures of these modified molecules are shown in FIG. 3a. Propyl-HDC was also modified by changing the length and structure of the carbon chains at both ends of the molecule (FIG. 3b), or polymerizing by joining the molecules at the two ends through carbon chains.

Results and Discussions

As shown in FIG. 2a, the redox potential of 1,4-DHAQ is 1.01 V vs. SHE, which matches with that of $\text{VO}^{2+}/\text{VO}_2^+$ (1.01V vs. SHE). As shown in FIG. 2b, the redox potential of both Propyl-HDC and $\text{VO}^{2+}/\text{VO}_2^+$ are 1.01 V vs. SHE. This makes them suitable to be used as capacity boosters for the $\text{VO}^{2+}/\text{VO}_2^+$ electrolyte.

Both 1,4-DHAQ and Propyl-HDC molecules show identical redox potentials to $\text{VO}^{2+}/\text{VO}_2^+$. This indicates that these two molecules have a great potential to be used as capacity booster in redox-targeting based $\text{VO}^{2+}/\text{VO}_2^+$ electrolyte from the perspective of potential matching.

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All other anthraquinone derivatives (i.e., 1,2-DHAQ, 1,5-DHAQ, 1,8-DHAQ) show a matched potential with $\text{VO}^{2+}/\text{VO}_2^+$. Propyl-HDC was also modified by changing the length and structure of the carbon chains at both ends of the molecule (FIG. 3b), or polymerizing by joining the molecules at the two ends through carbon chains, to reduce its solubility and

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Example 3: Boosting the Capacity upon Addition of the Capacity Boosters to the $\text{VO}^{2+}/\text{VO}_2^+$ Electrolyte

Capacity boosting upon addition of the above solid materials in $\text{VO}^{2+}/\text{VO}_2^+$ electrolyte is demonstrated. With 2,5-dichloro-1,4-phenylene bis((propylsulfonyl)amide) as an example, the performance of capacity booster in battery was tested by galvanostatic charge/discharge of symmetric cells.

20 Preparation of a Symmetric Cell

With 15 mL 0.60 M VO^{2+} dissolved in 0.50 M H_2SO_4 as catholyte where the capacity is limited and 15 mL 0.60 M VO^{2+} and 30 mL 0.60 M VO_2^+ dissolved in 0.50 M H_2SO_4 as anolyte, a symmetric cell was constructed.

25 Addition of Solid Material Granules with Capacity Booster into the Symmetric Cell

Solid material granules with capacity booster (containing 0.5 g Propyl-HDC active material, carbon black and binder) were added into the cathodic tank after several cycles and an obvious capacity increase was observed, which demonstrates the role of the capacity booster.

30

Results and Discussions

FIG. 4a shows the change in battery capacity before and after the addition of the capacity booster. The voltage profiles in different numbers of cycles are depicted in FIG. 4b, where the extended capacity in the voltage profile after the addition of the capacity booster can be

35

seen.

- Based on the changes in capacity before and after the addition of 0.5 g Propyl-HDC material in the tank, it can be concluded that the capacity booster exhibits a reversible specific capacity of 114 mAh/g. Compared to its theoretical capacity, it can be concluded that the material has a utilization rate of 82%. At the same time, there is no obvious material degradation (some fluctuations in capacity are due to crossover of vanadium species in the electrolytes).
- 5

CLAIMS

1. A composite material suitable for boosting the capacity of a $\text{VO}^{2+}/\text{VO}_2^+$ electrolytic flow cell battery, the composite material comprising:
- a capacity boosting material for a $\text{VO}^{2+}/\text{VO}_2^+$ flow cell;
 - a carbon black; and
 - a binder,

wherein:

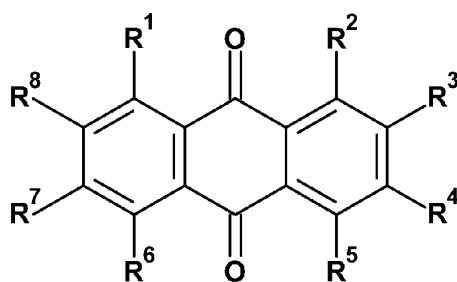
the capacity boosting material for a $\text{VO}^{2+}/\text{VO}_2^+$ flow cell is a material that is insoluble or is poorly soluble in an electrolyte suitable for use in a $\text{VO}^{2+}/\text{VO}_2^+$ flow cell; and

the capacity boosting material for a $\text{VO}^{2+}/\text{VO}_2^+$ flow cell is a material that has a redox potential that is about the same as the redox potential of $\text{VO}^{2+}/\text{VO}_2^+$, as measured relative to a standard hydrogen electrode.

2. The composite material according to Claim 1, wherein the capacity boosting material has a redox potential that is within 5% of the redox potential of $\text{VO}^{2+}/\text{VO}_2^+$, as measured relative to a standard hydrogen electrode.

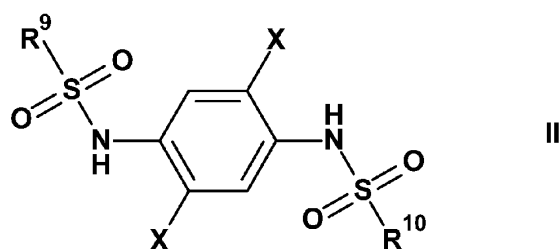
3. The composite material according to Claim 2, wherein the capacity boosting material has a redox potential that is identical to the redox potential of $\text{VO}^{2+}/\text{VO}_2^+$, as measured relative to a standard hydrogen electrode.

4. The composite material according to any one of the preceding claims, wherein the capacity boosting material has the formula I or the formula II:



I

; or



where:

R^1 to R^8 are each independently selected from H, C_1 to C_{10} alkyl or OH, provided that at two of R^1 to R^8 are OH;

R^9 and R^{10} are each independently selected from a C_1 to C_{20} alkyl group, an aryl group or a heteroaryl group, where each of the aryl and heteroaryl groups are unsubstituted or substituted by one or more groups selected from methyl, ethyl, methoxy, nitro and halo; and

X is independently selected from Cl, Br, F, or

the capacity boosting material is a polymeric material derived from the compound of formula II.

5. The composite material according to Claim 4, wherein the capacity boosting material is selected from one or more of the group consisting of:

- (a) 2,5-dichloro-1,4-phenylene bis((propylsulfonyl)amide);
- (b) 1,4-dihydroxyanthraquinone;
- (c) 1,2-dihydroxyanthraquinone;
- (d) 1,5-dihydroxyanthraquinone; and
- (e) 1,8-dihydroxyanthraquinone.

6. The composite material according to Claim 5, wherein the capacity boosting material is selected from one or more of the group consisting of:

- (a) 2,5-dichloro-1,4-phenylene bis((propylsulfonyl)amide); and
- (b) 1,4-dihydroxyanthraquinone.

7. The composite material according to any one of the preceding claims, wherein the composite material is insoluble or is poorly soluble in an electrolyte suitable for use in a VO^{2+}/VO_2^+ electrolytic flow cell.

8. A $\text{VO}^{2+}/\text{VO}_2^+$ flow cell battery comprising a capacity boosting material that has a redox potential that is about the same as the redox potential of $\text{VO}^{2+}/\text{VO}_2^+$, as measured relative to a standard hydrogen electrode.

9. The flow cell battery according to Claim 8, wherein the flow cell comprises:

a catholyte tank;

an anolyte tank; and

a redox flow cell comprising a cathode compartment, having a cathode electrode, and an anode compartment, having an anode electrode, separated by an ion selective membrane, where the cathode electrode and anode electrode are connectable to an energy harvesting or utilising device, where

the catholyte tank comprises the capacity boosting material as defined in Claim 8, $\text{VO}^{2+}/\text{VO}_2^+$, water and an acidic electrolyte support, and the catholyte tank is fluidly connected to the cathode compartment of the redox flow cell; and

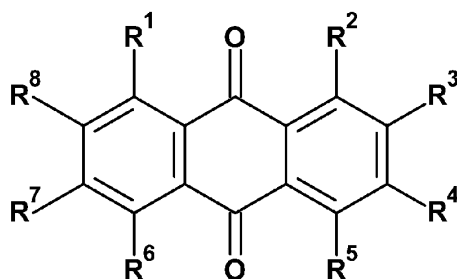
the anolyte tank comprises a different redox couple with a lower redox potential than $\text{VO}^{2+}/\text{VO}_2^+$, water and an acidic electrolyte support, and the anolyte tank is fluidly connected to the anode compartment of the redox flow cell.

10. The flow cell battery according to Claim 8 or Claim 9, wherein one or more of the following apply:

the capacity boosting material for a $\text{VO}^{2+}/\text{VO}_2^+$ flow cell is a material that is insoluble or is poorly soluble in an electrolyte suitable for use in a $\text{VO}^{2+}/\text{VO}_2^+$ flow cell; and

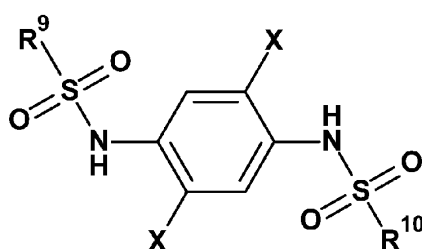
the capacity boosting material has a redox potential that is within 5% of the redox potential of $\text{VO}^{2+}/\text{VO}_2^+$, as measured relative to a standard hydrogen electrode (e.g. the capacity boosting material has a redox potential that is identical to the redox potential of $\text{VO}^{2+}/\text{VO}_2^+$, as measured relative to a standard hydrogen electrode).

11. The flow cell battery according to any one of Claims 8 to 10, wherein the capacity boosting material has the formula I or the formula II:



I

; or



II

where:

R¹ to R⁸ are each independently selected from H, C₁ to C₁₀ alkyl or OH, provided that at two of R¹ to R⁸ are OH;

R⁹ and R¹⁰ are each independently selected from a C₁ to C₂₀ alkyl group an aryl group or a heteroaryl group, where each of the aryl and heteroaryl groups are unsubstituted or substituted by one or more groups selected from methyl, ethyl, methoxy, nitro and halo; and

X is independently selected from Cl, Br, F, or

the capacity boosting material is a polymeric material derived from the compound of formula II.

12. The flow cell battery according to Claim 11, wherein the capacity boosting material is selected from one or more of the group consisting of:

- (a) 2,5-dichloro-1,4-phenylene bis((propylsulfonyl)amide);
- (b) 1,4-dihydroxyanthraquinone;
- (c) 1,2-dihydroxyanthraquinone;
- (d) 1,5-dihydroxyanthraquinone; and
- (e) 1,8-dihydroxyanthraquinone, optionally wherein the capacity boosting material is selected from one or more of the group consisting of:

- (a) 2,5-dichloro-1,4-phenylene bis((propylsulfonyl)amide); and
- (b) 1,4-dihydroxyanthraquinone.

13. The flow cell battery according to any one of Claims 8 to 12, wherein the capacity boosting material is provided in a composite material as described in any one of Claims 1 to 7.

14. The flow cell battery according to any one of Claims 8 to 13, wherein the different redox couple with a lower redox potential than $\text{VO}^{2+}/\text{VO}_2^+$ is selected from one or more of the group consisting of $\text{V}^{2+}/\text{V}^{3+}$, $\text{TiO}^{2+}/\text{Ti}^{3+}$, H_2/H^+ , and $\text{Cr}^{2+}/\text{Cr}^{3+}$.

15. A method of using a capacity boosting material suitable for boosting the capacity of a $\text{VO}^{2+}/\text{VO}_2^+$ flow cell battery, the method comprising the steps of:

- (a) providing a $\text{VO}^{2+}/\text{VO}_2^+$ flow cell battery, the battery comprising
 - a catholyte tank;
 - an anolyte tank; and
 - a redox flow cell comprising a cathode compartment, having a cathode electrode, and an anode compartment, having an anode electrode, separated by an ion selective membrane, where the cathode electrode and anode electrode are connectable to an energy harvesting or utilising device, where
 - the catholyte tank comprises:
 - a capacity boosting material that has a redox potential that is about the same as the redox potential of $\text{VO}^{2+}/\text{VO}_2^+$, as measured relative to a standard hydrogen electrode;
 - $\text{VO}^{2+}/\text{VO}_2^+$; and
 - a catholyte comprising water and an acidic electrolyte support, and the catholyte tank is fluidly connected to the cathode compartment of the redox flow cell; and
 - the anolyte tank comprises a different redox couple with a lower redox potential than $\text{VO}^{2+}/\text{VO}_2^+$, water and an acidic electrolyte support, and the anolyte tank is fluidly connected to the anode compartment of the redox flow cell; and
- (b) operating the battery to generate electricity through cycling the catholyte and anolyte from the catholyte and anolyte tanks into the cathode and anode compartments, respectively, and returning the catholyte and anolyte to the catholyte and anolyte tanks, respectively in a continuous sequence until the battery is discharged,
 - wherein, in a charged state, VO_2^+ is the predominant form of the $\text{VO}_2^+/\text{VO}_2^+$ and the capacity boost material is predominantly in a reduced state, and in a fully discharged state

VO^{2+} is the predominant form of the $\text{VO}_2^+/\text{VO}_2^+$ and the capacity boost material is predominantly in an oxidised state.

16. A method of charging a $\text{VO}^{2+}/\text{VO}_2^+$ flow cell battery as described in Claim 15 wherein the method comprises applying electricity to the flow cell and cycling the catholyte and anolyte from the catholyte and anolyte tanks into the cathode and anode compartments, respectively, and returning the catholyte and anolyte to the catholyte and anolyte tanks, respectively in a continuous sequence until the battery is charged, wherein in a fully discharged state VO^{2+} is the predominant form of the $\text{VO}_2^+/\text{VO}_2^+$ and the capacity boost material is predominantly in an oxidised state and in a charged state, VO_2^+ is the predominant form of the $\text{VO}_2^+/\text{VO}_2^+$ and the capacity boost material is predominantly in a reduced state.

17. The method according to Claim 15 or Claim 16, wherein the different redox couple with a lower redox potential than $\text{VO}^{2+}/\text{VO}_2^+$ is selected from one or more of the group consisting of $\text{V}^{2+}/\text{V}^{3+}$, $\text{TiO}^{2+}/\text{Ti}^{3+}$, H_2/H^+ , and $\text{Cr}^{2+}/\text{Cr}^{3+}$.