[0005] The high solubility of halides, particularly chlorine and bromine, in aqueous solution, leads to critical technical challenges in halide-based batteries, as the crossover of the halide from the cathode to the anode causes self-discharge and reduces battery efficiency. The battery must therefore contain some means for confining the halide to the cathode side of the battery. One known example of such a means is a semipermeable barrier, which permits the exchange of electrolyte ions but not of the halogen. However, such existing systems have numerous disadvantages.

[0006] For example, in the past a microporous membrane has been typically used to reduce crossover of halide from the cathode side of the battery to the anode side. An alternative option has been to use an ion-exchange membrane, which is an ionically conductive but electrically non-conductive barrier. These may be used in conjunction with a molecular complexing agent dissolved in the electrolyte such as MEPBr. However, existing systems utilizing a microporous battery membrane or an ion-exchange membrane, and/or dissolved molecular complexing agent have a number of disadvantages including the high cost of existing membrane materials (in particular ion-exchange membranes), the accumulation of a high concentration of complexed polybromide ions which forms an oily phase near the cathode, and insufficient suppression of bromine crossover.

[0007] Therefore, there is a need for a means of confining the halogen to the cathode side of the battery, without the disadvantages which accompany existing systems. An object of the present invention is to overcome one or more of the disadvantages of existing systems such as those outlined above.

Summary

[0008] In a first aspect of the disclosure, there is provided a battery, comprising an anode, a cathode, an electrolyte disposed between the anode and the cathode, a halogen in contact with the cathode, and a metal in contact with the anode, wherein the halogen is in contact with a polymeric halogen sequestering agent (HSA) which is a polymer comprising a moiety capable of sequestering the halogen.

[0009] The following options may be used in conjunction with the first aspect, either individually or in any suitable combination.

[00010] During discharge the halogen may be reduced at the cathode and the metal may be oxidised at the anode.

[00011] The halogen may be complexed with the polymeric HSA.

[00012] There is also provided a discharged battery, comprising an anode, a cathode, an electrolyte, a halide, wherein the halide is in contact with the cathode, and a metal cation, wherein the metal cation is in contact with the anode, wherein the halide is in contact with the polymeric halogen sequestering agent (HSA), which is a polymer comprising a moiety capable of sequestering the halogen of the halide.

[00013] The following options may be used in conjunction with the above, either individually or in any suitable combination.

[00014] During charging the halide may be oxidised at the cathode and the metal may be reduced at the anode.

[00015] The following options may be used in conjunction with the above, either individually or in any suitable combination.

[00016] The moiety capable of sequestering the halogen may be a quaternary ammonium halide group, a phosphonium halide group, or a sulfonium halide group. The moiety capable of sequestering the halogen may be a quaternary ammonium halide group.

[00017] The electrolyte may be an aqueous electrolyte. Alternatively, the electrolyte may be a non-aqueous electrolyte. The electrolyte may be a gel electrolyte.

[00018] The battery may further comprise at least one semipermeable barrier disposed between the anode and the cathode. In this case, the polymeric HSA may be disposed on the at least one semipermeable barrier. The polymeric HSA may be disposed on a cathode-facing surface of the semipermeable barrier or an anode-facing surface of the semipermeable barrier, or on both faces of the semipermeable barrier. The polymeric HSA may be distributed throughout the semipermeable barrier. The battery may comprise two or more semipermeable barriers disposed between the anode and the cathode. Alternatively, the battery may comprise no more than one semipermeable barrier which is a spacer. The battery may comprise no more than two

(hydroxymethyl)propane tri(meth)acrylate, triallyl cyanurate, triallyl isocyanurate, triallyl trimellitate, diallyl phthalate, diallyl terephthalate, divinyl benzene, methylol (meth)acrylamide, triallylamine, oleyl maleate, glyceryl propoxy triacrylate, allyl methacrylate, methacrylic anhydride and methylenebis(meth)acrylamide.

[00032] The polymeric HSA may be not soluble in the electrolyte. Alternatively, the polymeric HSA may be soluble in the electrolyte.

[00033] In the battery of the disclosure, the oxidant crossover may be reduced by up to 70% over 5 hours compared to an equivalent battery without a polymeric HSA, as measured by discharge of the battery.

[00034] There is also provided use of a polymeric HSA to reduce oxidant crossover in a battery; wherein the battery comprises an anode, a cathode, an electrolyte disposed between the anode and the cathode, a halogen in contact with the cathode, and a metal in contact with the anode; and wherein the halogen is in contact with a polymeric halogen sequestering agent (HSA) which is a polymer comprising a moiety capable of sequestering the halogen.

[00035] There is also provided use of a polymeric halogen sequestering agent (HSA) which is a polymer comprising a moiety capable of sequestering a halogen, in the production of a battery, wherein the battery comprises an anode, a cathode, an electrolyte disposed between the anode and the cathode, a halogen in contact with the cathode, and a metal in contact with the anode; wherein the halogen is in contact with the polymeric HSA.

[00036] There is also provided a method of producing a battery, the method comprising providing an anode and a cathode, providing an electrolyte disposed between the anode and the cathode, placing a metal in contact with the anode, and placing the halogen in contact with the cathode and in contact with a polymeric halogen sequestering agent (HSA) which is a polymer comprising a moiety capable of sequestering a halogen.

[00037] The following options may be used in conjunction with the above, either individually or in any suitable combination.

ethyl-4-vinyl pyridinium halide (EVP). The polymeric HSA may be a polymer or co-polymer of diallyldimethyl ammonium halide (DADMAC).

[00053] The polymeric HSA may be a co-polymer or graft polymer of at least two different compounds of Formula (I), Formula (II), Formula (III), and/or Formula (IV). The polymeric HSA may be a co-polymer of diallyldimethyl ammonium halide (DADMAC) and triallymethyl ammonium halide (TAMA).

[00054] The polymeric HSA may comprise a functional co-monomer. The functional co-monomer may be selected from the group consisting of 2-hydroxyethyl acrylate (HEA), acrylamide, and glycidyl methacrylate (GMA).

[00055] The polymeric HSA may also comprise a cross-linker. The cross-linker may be selected from the group consisting of bisacrylamide, ethylene glycol dimethylacrylate, tetraallyl piperazinium halide salts, tetraallyl ammonium halide salts, tetraallylethylenediamine and quaternized halide salts thereof, 1,3-bis(diallylamino) propane and quaternized halide salts thereof, ethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, 1,3-butylene glycol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, l,4-butanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, pentaerythritol di(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, glycerol di(meth) acrylate, glycerol allyloxy di(meth)acrylate, (hydroxymethyl)ethane di(meth)acrylate, l,l,l-tris (hydroxymethyl)ethane tri(meth)acrylate, l,l,l-tris (hydroxymethyl)propane di(meth)acrylate, l,l,l-tris (hydroxymethyl)propane tri(meth)acrylate, triallyl cyanurate, triallyl isocyanurate, triallyl trimellitate, diallyl phthalate, diallyl terephthalate, divinyl benzene, methylol (meth)acrylamide, triallylamine, oleyl maleate, glyceryl propoxy triacrylate, allyl methacrylate, methacrylic anhydride and methylenebis(meth)acrylamide.

[00056] In the battery of the disclosure, the oxidant crossover may be reduced by up to 70% over 5 hours compared to an equivalent battery without a polymeric HSA, as measured by discharge of the battery.

[00057] The halide may be selected from the group consisting of F^-, Cl^-, Br^- and I^-. The halide may be Br^-. The metal cation may be selected from the group consisting of Zn^{2+}, Mg^{2+}, Li^+, K^+, Ca^{2+}, Fe^{3+}, Fe^{2+}, Ni^{3+}, and Al^{3+}. The metal cation may be Zn^{2+}.

CLAIMS

1. A battery, comprising

an anode,

a cathode,

an electrolyte disposed between the anode and the cathode,

a halogen in contact with the cathode, and

a metal in contact with the anode,

wherein the halogen is in contact with a polymeric halogen sequestering agent (HSA) which is a polymer comprising a moiety capable of sequestering the halogen.

2. The battery of claim 1, wherein the moiety capable of sequestering the halogen is a quaternary ammonium halide group, a phosphonium halide group, or a sulfonium halide group, preferably a quaternary ammonium halide group.

3. The battery of claim 1 or claim 2, wherein the cathode comprises a cathode active layer, wherein the polymeric HSA is distributed in and/or on the cathode active layer, and wherein the cathode active layer comprises a carbon material having a surface area greater than 70 cm^2/cm^3.

4. The battery of claim 3, wherein the cathode active layer comprises carbon felt, carbon foam, packed carbon powder, expanded graphite, aerogel carbon, xerogel carbon, or sol-gelated carbon, preferably carbon felt or packed carbon powder.

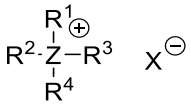
5. The battery of claim 3 or claim 4, wherein the cathode active layer comprises packed carbon powder which is activated carbon, carbon black, expanded graphite, graphite, or a combination of two or more thereof.

6. The battery of any one of claims 3 to 5, wherein the cathode active layer comprises packed carbon powder and does not comprise a polymeric binder.

7. The battery of any one of claims 1 to 6, wherein the metal is Zn.

8. The battery of any one of claims 1 to 7, wherein the halogen is bromine.

9. The battery of any one of claims 1 to 8, wherein the polymeric HSA is a polymer or co-polymer of a compound of Formula (I):


, wherein

Z is N, P or S,

R^1 is allyl or vinyl,

R^2 is selected from the group consisting of allyl, vinyl, and optionally substituted branched or unbranched C_1 to C_{18} alkyl, and X^- is Cl^-, I^-, Br^-, F^-, SCN^-, OCN^-, OH^-, $C_2O_4^{2-}$, $HCOO^-$, HCO_3^-, CO_3^{2-}, OCl^-, OBr^-, BrO_3^- , ClO_3^-, SO_3^{2-}, NO^{2-}, IO_3^- , $H_2PO_4^-$, HPO_4^{2-}, SO_4^- , NO_3^-, ClO_4^-, bis(trifluoromethylsulfonyl)-imide, bis(fluorosulfonyl)imide, hexafluorophosphate, tetrafluoroborate, tris(pentafluoro)trifluorophosphate, acetate, propionate, pentanoate, hexanoate, or a combination thereof, or

R^2 and X^- are absent, and

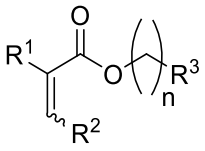
R^3 and R^4 are each independently selected from allyl, vinyl, optionally substituted branched or unbranched C_1 to C_{18} alkyl, or

R^3 and R^4 are joined to form a 4, 5, or 6-membered ring together with Z, optionally comprising one or more heteroatoms selected from the group consisting of O, P and N, wherein said ring is optionally substituted,

wherein each optional substituent is independently selected from the group consisting of allyl, vinyl, branched and unbranched C_1 to C_{18} alkyl, Cl, Br, I, F, $-OR^5$, $-NR^5R^6$, $-N^+R^5R^6R^7$, $-SR^5$, $-COOR^5$, and carbonyl,

wherein R^5, R^6 and R^7 are each independently selected from branched or unbranched C_1 to C_{18} alkyl or H, and any two of R^5, R^6 and R^7 are optionally joined to form a 4, 5, or 6-membered ring together with N.

10. The battery of any one of claims 1 to 8, wherein the polymeric HSA is a polymer or co-polymer of a compound of Formula (II):



, wherein

R^1 is H or methyl,

R^2 is H or $CH_2Z^+R^4R^5R^6X^-$,

wherein when R^2 is H, R^3 is $CH_2Z^+R^4R^5R^6X^-$, and when R^2 is $CH_2Z^+R^4R^5R^6X^-$, R^3 is branched or unbranched C_1 to C_{12} alkyl, and

wherein R^4, R^5 and R^6 are independently selected from branched or unbranched C_1 to C_{12} alkyl, or R^4 and R^5 are joined to form a 5, or 6-membered ring together with Z and R^6 is branched or unbranched C_1 to C_{12} alkyl, and

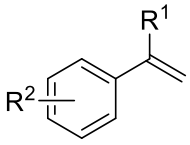
wherein X^- is Cl^-, I^-, Br^-, F^-, SCN^-, OCN^-, OH^-, $C_2O_4^{2-}$, $HCOO^-$, HCO_3^-, CO_3^{2-}, OCl^-, OBr^-, BrO_3^-, ClO_3^-, SO_3^{2-}, NO^{2-}, IO_3^-, $H_2PO_4^-$, HPO_4^{2-}, SO_4^-, NO_3^-, ClO_4^-, bis(trifluoromethylsulfonyl)-imide, bis(fluorosulfonyl)imide, hexafluorophosphate, tetrafluoroborate, tris(pentafluoro)trifluorophosphate, acetate, propionate, pentanoate, hexanoate, or a combination thereof, or

R^6 and X^- are absent,

wherein Z is N, P or S, and

n is 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12.

11. The battery of any one of claims 1 to 8, wherein the polymeric HSA is a polymer or co-polymer of a compound of Formula (III):



, wherein

R^1 is H or methyl, and

R^2 is $CH_2Z^+R^3R^4R^5X^-$ or $Z^+R^3R^4R^5X^-$,

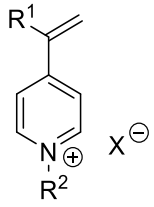
wherein R^3, R^4 and R^5 are independently selected from branched or unbranched C_1 to C_{12} alkyl, or R^3 and R^4 are joined to form a 5, or 6-membered ring together with Z and R^5 is branched or unbranched C_1 to C_{12} alkyl, and

wherein X^- is Cl^-, I^-, Br^-, F^-, SCN^-, OCN^-, OH^-, $C_2O_4^{2-}$, $HCOO^-$, HCO_3^-, CO_3^{2-}, OCl^-, OBr^-, BrO_3^-, ClO_3^-, SO_3^{2-}, NO^{2-}, IO_3^-, $H_2PO_4^-$, HPO_4^{2-}, SO_4^-, NO_3^-, ClO_4^-, bis(trifluoromethylsulfonyl)-imide, bis(fluorosulfonyl)imide, hexafluorophosphate, tetrafluoroborate, tris(pentafluoro)trifluorophosphate, acetate, propionate, pentanoate, hexanoate, or a combination thereof, or

R^5 and X^- are absent, and

wherein Z is N, P or S.

12. The battery of any one of claims 1 to 8, wherein the polymeric HSA is a polymer or co-polymer of a compound of Formula (IV):



, wherein

R^1 is H or methyl,

R^2 is optionally substituted branched or unbranched C_1 to C_{18} alkyl,

wherein each optional substituent is independently selected from the group consisting of vinyl, allyl, branched and unbranched C_1 to C_{18} alkyl, Cl, Br, I, F, $-OR_5$, $-NR^5R^6$, $-N^+R^5R^6R^7$, $-SR_5$, $-COOR_5$, and carbonyl,

wherein R^5, R^6 and R^7 are each independently selected from branched or unbranched C_1 to C_{18} alkyl or H, and any two of R^5, R^6 and R^7 are optionally joined to form a 4, 5, or 6-membered ring together with N, and

X^- is Cl^-, I^-, Br^-, F^-, SCN^-, OCN^-, OH^-, $C_2O_4^{2-}$, $HCOO^-$, HCO_3^-, CO_3^{2-}, OCl^-, OBr^-, BrO_3^-, ClO_3^-, SO_3^{2-}, NO^{2-}, IO_3^-, $H_2PO_4^-$, HPO_4^{2-}, SO_4^-, NO_3^-, ClO_4^-, bis(trifluoromethylsulfonyl)-imide, bis(fluorosulfonyl)imide, hexafluorophosphate, tetrafluoroborate, tris(pentafluoro)trifluorophosphate, acetate, propionate, pentanoate, hexanoate, or a combination thereof.

13. The battery of any one of claims 1 to 40, wherein the polymeric HSA is a polymer or co-polymer of a compound selected from the group consisting of diallyldimethyl ammonium halide (DADMAC), triallymethyl ammonium halide (TAMA), triallyl (2-hydroxyethyl) ammonium

halide (TAHEA), diallyl ethyl (2-hydroxy ethyl) ammonium halide (DAEHEA), 1-(2-hydroxyethyl)-4-vinyl pyridinium halide (HEVP), 1-ethyl-4-vinyl pyridinium halide (EVP), vinylalkylpyrrolidinium halide (VAP), vinylpyrrolidone, allylalkylpyrrolidionium halide, diallylpyrrolidinium halide, N,N-dimethylaminoethyl methacrylate, N,N-diethylaminoethyl methacrylate, [2-(methacryloyloxy)ethyl]trimethylammonium halide, [2-(methacryloyloxy)ethyl]triethylammonium halide, N,N-dimethylaminoethyl acrylate, N,N-diethylaminoethyl acrylate, [2-(acryloyloxy)ethyl]trimethylammonium halide, [2-(acryloyloxy)ethyl]triethylammonium halide, dimethylamino alpha-methylstyrene and isomers and methyl halide quaternary salts thereof, diethylamino alpha-methylstyrene and isomers and ethyl halide quaternary salts thereof, (vinylbenzyl)trimethylammonium halide, (vinylbenzyl)triethylammonium halide, (vinylbenzyl)dimethylamine, (vinylbenzyl)diethylamine, tetraallyl ammonium halide (TAA), and tetraallyl piperazinium halide (TAP).

14. The battery of any one of claims 1 to 13, wherein the polymeric HSA is a co-polymer or graft polymer of at least two different compounds of Formula (I), Formula (II), Formula (III), and/or Formula (IV) , and/or wherein the polymeric HSA also comprises a cross-linker, preferably wherein the cross-linker is selected from the group consisting of bisacrylamide, ethylene glycol dimethylacrylate, tetraallyl piperazinium halide salts, tetraallyl ammonium halide salts, tetraallylethylenediamine and quaternized halide salts thereof, 1,3-bis(diallylamino) propane and quaternized halide salts thereof, ethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, 1,3-butylene glycol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, l,4-butanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, pentaerythritol di(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, glycerol di(meth) acrylate, glycerol allyloxy di(meth)acrylate, (hydroxymethyl)ethane di(meth)acrylate, l,l,l-tris (hydroxymethyl)ethane tri(meth)acrylate, l,l,l-tris (hydroxymethyl)propane di(meth)acrylate, l,l,l-tris (hydroxymethyl)propane tri(meth)acrylate, triallyl cyanurate, triallyl isocyanurate, triallyl trimellitate, diallyl phthalate, diallyl terephthalate, divinyl benzene, methylol (meth)acrylamide, triallylamine, oleyl maleate, glyceryl propoxy triacrylate, allyl methacrylate, methacrylic anhydride and methylenebis(meth)acrylamide.

15. The battery of any one of claims 1 to 14, wherein oxidant crossover is reduced by up to 70% over 5 hours compared to an equivalent battery without a polymeric HSA, as measured by discharge of the battery.