[0030] In general, the electrolyte solutions of the present disclosure have a plating efficiency in the range of about 50% to about 100% , and in other aspects, in the range of from 75% to about 100%.

[0031] The foregoing plating efficiency parameters are as follows:

Test Conditions: 25°C;
2-electrode cell set-up;

Working Electrode:
Conductive graphite rod (d=0.635cm or 1/4 in, length 5cm, surface area~10cm^2)

Counter/Ref Electrode:
Conductive graphite rod (d=0.635cm or 1/4 inch)

Equipment: MTI battery tester

Electrolyte: 35mL 2.5M $ZnBr_2$, 0.05M Br_2 and 0.7M Polybromide complex

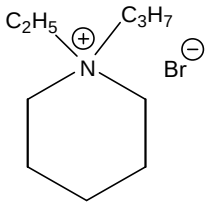
30mA for 5 hours (total ~150mAh plating capacity) non-stirred condition

Working electrodes were thoroughly cleaned by DI water rinse and dried after zinc plating. Zinc plated on working electrode was determined by measuring weight difference of working electrode before and after plating test. Zinc plating efficiencies were calculated by real zinc weight over theoretical zinc weight, which was obtained by Faraday's law of electrolysis assuming 100% conversion from 180mAh capacity.

[0032] The class A quat-containing electrolyte solutions of the present disclosure generally have cloud points (as defined herein) at temperatures of less than about 25°C, in some aspects, less than about 0°C, and in still other aspects, less than about -10°C. The electrolyte solutions of the present disclosure comprising both class A and class B quats generally have cloud points of less than about 25°C, with some mixtures exhibiting cloud points of less than 5°C.

[0033] The forward operation of a bromine-containing battery generally involves the conversion of elemental bromine to ionic bromine. The quat/Br_2 complex results from an equilibrium reaction in which the Br_2 is released from the complex as the concentration of free Br_2 in the aqueous electrolyte drops during battery operation. In its fully charged state, the electrolyte solution inevitably contains some degree of uncomplexed bromine. A measure of a quat's ability to complex elemental bromine is the amount of elemental bromine left in solution when the complexation reaction proceeds to equilibrium. Such

or



[0038] The complexing agents can be used in membraneless aspects. In one aspect, the present disclosure provides a membraneless flow cell battery comprising an electrolyte solution comprising one or more class A quat halides, or a mixture of one or more class A quat halides and one or more class B quat halides

EXAMPLES

Example 1

Measurement of free bromine in aqueous phase:

Two slightly different methods were used to prepare the electrolyte compositions, A) one containing 0.7M quat and B) the other containing 0.8M quat. In composition A, 2.0 moles of bromine was added to an aqueous solution containing 0.5 moles of zinc bromide and 0.7 moles of the quat. The two-phase mixture was stirred for 24 hrs. and then the phases were allowed to settle. The top aqueous phase was sampled for free bromine measurement. In composition B, 1.44 moles of bromine was added to an aqueous solution containing 0.5 moles of zinc bromide, 0.4 moles of zinc chloride and 0.8 moles of the quat. The top aqueous phase obtained after stirring for 24 hrs. was used for free bromine measurement.

A 250-ml Erlenmeyer flask was charged with 50 ml of deionized water and weighed (A). A sample of the clear aqueous phase was passed through glass wool to remove any suspended organic phase and then added to the Erlenmeyer flask. The flask was weighed again (B) and the difference in weight (B-A) was noted as the weight of the sample. About 20 ml of 20% potassium iodide solution followed by about 5 ml of starch solution was added to the flask. The resulting dark mixture was titrated against 0.02N sodium thiosulfate solution. The end-point was the disappearance of purple color. Free bromine (wt%) was calculated in the following manner:

Wt% free Br_2 = Volume (ml) of sodium Thiosulfate x Normality of Sodium thisosulfate/ Sample Weight.

Example 2

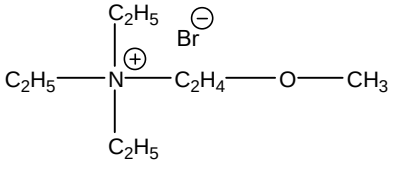
Cloud point determination:

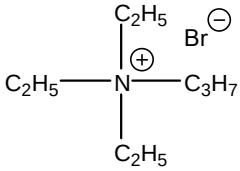
1. A 0.7M quaternary ammonium bromide in 2.5M Zinc Bromide water solution was prepared.
2. The solution was transferred to a jacketed flask with a stirring bar and temperature monitor.
3. The solution was warmed to 15°C above the expected cloud point. If necessary, any moisture or impurities were removed by filtration.
4. The solution was stirred, with speed adjustment to about 250 rpm, while avoiding the formation of bubbles.
5. The solution was cooled gradually (cooling rate of about 1°C/5min).
6. The sample was inspected carefully for signs of cloudiness, and the temperature at which cloudiness was observed was recorded to the nearest 0.1°C.

Note that step 3 may require the performance of an approximate cloud point measurement to roughly determine an expected cloud point. Such a measurement can be performed preparing a solution as in steps 1 and 2, and subjecting it to a temperature drop from an initial temperature which is higher than any expected cloud point, such as, for example, about 45°C.

Examples 3-7 and 9: The cloud points and free bromine were measured as in Examples 1 and 2, respectively

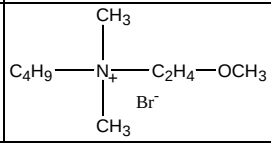
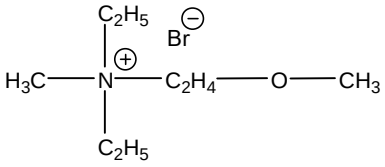
Example 3

	Name	Structure	MW	Solubility in $ZnBr_2$ Cloudy Point	Free Br_2
2	Triethylether Quat Bromide		240	0.7M, <-10.5°C	0.7M 0.658%

5	Triethylpropyl Quat Bromide		224	0.7M, 41.2°C	0.7M 0.089%
6	Mixture 50/50 mol% of 2 and 5		232	0.7M, 10.5°C	0.7M 0.25%

The free bromine of compound 2 at 0.7M is 0.658%, and that of compound 5 is 0.089%. Nevertheless, the 50/50 mol% ratio of the two compounds has a free bromine of 0.25% at 0.7M, which is a drop in free bromine of significantly more than 50% with respect to the free bromine of the triethylether quat alone.

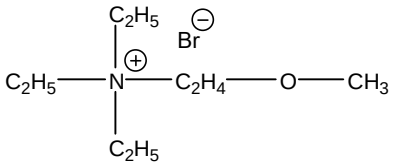
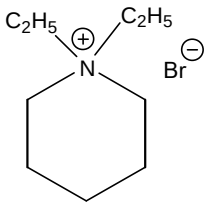
Example 4

	Name	Structure	MW	Solubility in $ZnBr_2$ Cloud Point	Free Br_2
1	Dimethylbutylether Quat Bromide		240	0.7M, 29°C	0.7M 0.28%
4	Diethylmethylether Quat Bromide		226	0.7M, < -10.5°C	0.7M 0.70%
7	Mixture 50/50 mol% of 1 and 4		233	0.7M, 9°C	0.7M 0.22%

Note that compound 4 differs from compound 1 only in having 1 less carbon atom on one of its methyl groups. The free bromine at 0.7M can be expected to be higher to that of compound 1.

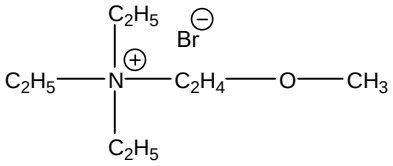
Nevertheless, the 50/50 mol% ratio of the two compounds has a free bromine of 0.22% at 0.7M, which is similar to that of compound 1.

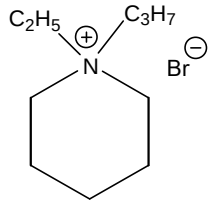
Example 5

	Name	Structure	MW	Solubility in $ZnBr_2$ Cloud Point	Free Br_2
2	Triethylether Quat Bromide		240	0.7M, < -10.5°C	0.8M 0.467%
9	Diethyl Piperidinium Bromide		222	0.7M, 11.9 °C	0.8M 0.26%
12	Mixture 50/50 mol% of 2 and 9		231	0.7M, -3 °C	0.8M 0.27%

The free bromine of compound 2 at 0.8M is 0.467%, and that of compound 9 at 0.8M is 0.26%. A 50/50 mol% ratio of the two compounds has a surprisingly low free bromine of 0.27% at 0.8M.

Example 6

	Name	Structure	MW	Solubility in $ZnBr_2$ Cloud Point	Free Br_2
2	Triethylether Quat Bromide		240	0.7M, < -10.5°C	0.8M 0.467%

10	EthylPropyl Piperidinium Bromide		236	0.7M, 45.8°C	0.8M 0.026%
13	Mixture 50/50 mol% of 2 and 10		238	0.7M, 18.8°C	0.8M 0.062%

The free bromine of compound 2 at 0.8M is 0.467%, and that of compound 10 at 0.8M is 0.026%. A 50/50 mol% ratio of the two compounds has a surprisingly low free bromine of 0.062% at 0.8M.

Example 7

Test Conditions: 25°C
2-electrode cell set-up
Working Electrode:
Conductive graphite rod (d=0.635cm or 1/4 in, length 5cm, surface area~10cm^2)
Counter/Ref Electrode:
Conductive graphite rod (d=0.635cm or 1/4 inch)

Equipment: MTI battery tester

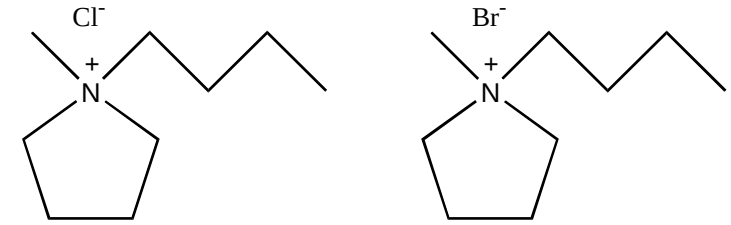
Electrolyte: 35mL 2.5m $ZnBr_2$, 0.05M Br_2 and 0.7M Polybromide complex

30mA for 5 hours (total ~150mAh plating capacity) non-stirred condition

Working electrodes were thoroughly cleaned by DI water rinse and dried after zinc plating. Zinc plated on working electrode was determined by measuring weight difference of working electrode before and after plating test. Zinc plating efficiencies were calculated by real zinc weight over theoretical zinc weight, which was obtained by Faraday's law of electrolysis assuming 100% conversion from 180mAh capacity.

Complexing Agent	Plating Efficiency
MEP	59.88%
Example-3 Blend	79.05%
Example-4 Blend	-
Example-5 Blend	74.65%
Example-6 Blend	98.38%

Example 8



Chloroquat Bromoquat

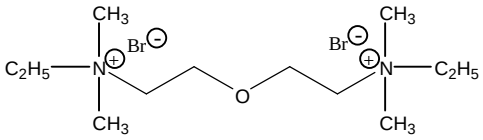
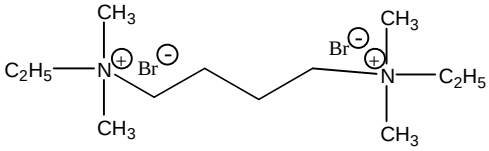
Chloride ions are added to the electrolyte in amounts sufficient to reduce the amount of free bromine present and increase the electrolyte conductivity during charging of the cell. Chloride ions in the electrolyte may come from zinc chloride or quaternary ammonium chloride complexing agent.

Experiment 1 of Example 8: An aqueous electrolyte system was prepared having 0.84 M zinc bromide, 0.8 M chloroquat (N-methyl, N-butyl pyrrolidinium chloride) and 1.44 M bromine. After the sample was stirred for 24 hrs at 35ºC, the amount of free bromine present in the electrolyte was 0.26%.

Experiment 2 of Example 8: An aqueous electrolyte system was prepared having 0.84 M zinc bromide, 0.8 M bromoquat (N-methyl, N-butyl pyrrolidinium bromide) and 1.44 M bromine. After the sample was stirred for 24 hrs at 35ºC, the amount of free bromine present in the electrolyte was 0.25%.

Component	Experiment 1	Experiment 2
	Concentration (M)	Concentration (M)
$ZnBr_2$	0.84	0.44
$ZnCl_2$	0	0.40
Br_2	1.44	1.44
Bromoquat	0	0.8
Chloroquat	0.8	0

Example 9

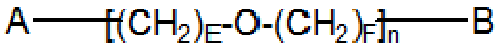
	Name	Structure	MW	Solubility in $ZnBr_2$ Cloud Point	Free Br_2
14	Dimethylethyl Gemini Quat Bromide with Diethylether Linkage		378	0.7M, 48.2°C	0.7M 0.71%
15	Dimethylethyl Gemini Quat Bromide with Butyl Linkage		362	0.7M, 89.2°C	0.7M 0.59%

The free bromine of compound 14 at 0.7 M is 0.71%, and that of compound 15 at 0.7 M is 0.59_%.

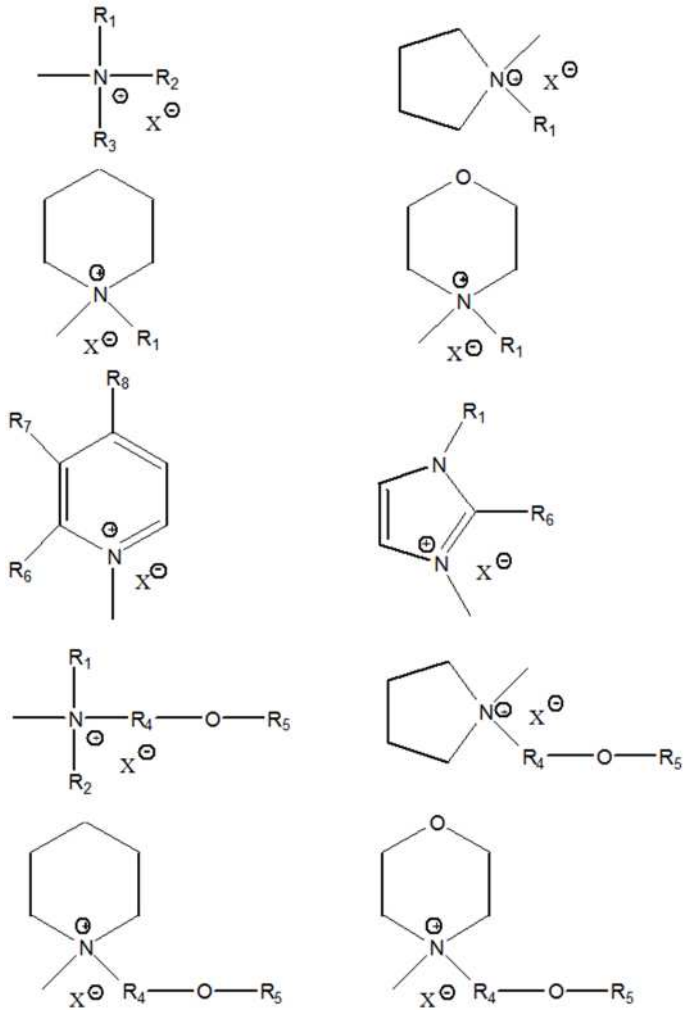
[0039] Components referred to by chemical name or formula anywhere in the specification or claims hereof, whether referred to in the singular or plural, are identified as they exist prior to coming into contact with another substance referred to by chemical name or chemical type (*e.g.*, another component, a solvent, or *etc*.). It matters not what chemical changes, transformations and/or reactions, if any, take place in the resulting mixture or solution as such changes, transformations, and/or reactions are the natural result of bringing the specified components together under the conditions called for pursuant to this disclosure. Thus the components are identified as ingredients to be brought together in connection with performing a desired operation or in forming a desired composition. Also, even though the claims hereinafter may refer to substances, components and/or ingredients in the present tense ("comprises", "is", *etc*.), the reference is to the substance, component or ingredient as it existed at the time just before it was first contacted, blended or mixed with one or more other substances, components and/or ingredients in accordance with the present disclosure. The fact that a substance, component or ingredient may have lost its original identity through a chemical reaction or transformation during the course of contacting, blending or mixing operations, if

CLAIMS

1. An electrolyte solution comprising one or more class A quat halides, each having a molecular structure selected from the group consisting of:



wherein A and B each are each independently selected from the group consisting of:



wherein

E and F are each independently in the range of 1 to 10;

n is in the range of 1 to 10;

X^- is Br^- or Cl^-, or the quat is a mixture of both bromides and chlorides;

R_1, R_2, R_3, are, independently, hydrogen or alkyl substituents having 12 or fewer carbon atoms;

R_4 is an alkyl chain having in the range of 1 to 10 carbon atoms;

R_5 is an alkyl group having in the range of 1 to 6 carbon atoms; and

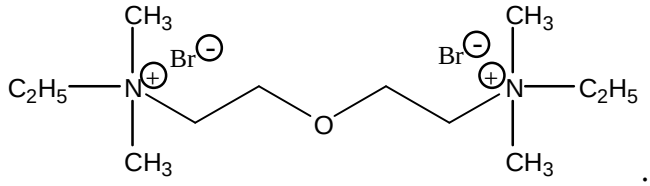
R_6, R_7 and R_8 are, independently, hydrogen or alkyl substituents having 12 or fewer carbon atoms.

2. An electrolyte solution as in claim 1 wherein R_1, R_2 and R_3 are, independently, hydrogen or alkyl substituents having in the range of 1 and 7 carbon atoms.

3. An electrolyte solution as in claim 1 wherein R_4 is an alkyl chain having in the range of 1 to 4 carbon atoms.

4. An electrolyte solution as in claim 1 wherein R_5 is an alkyl group having in the range of 1 to 4 carbon atoms.

5. An electrolyte solution as in claim 1 wherein the one or more class A quats is/are dimethylethyl gemini quat bromide with diethylether linkage having the following structure:



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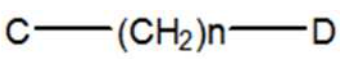
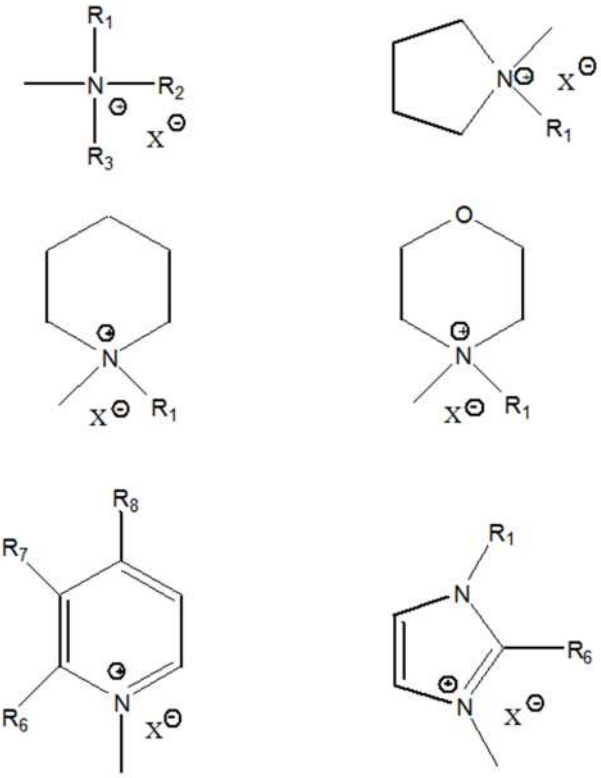
6. An electrolyte solution as in claim 1 further comprising one or more class B quats, each having the following structure:



wherein C and D each are each independently selected from the group consisting of:



wherein

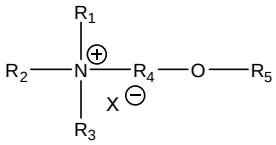
X^- is Br- or Cl-, or the quat is a mixture of both bromides and chlorides;

n is in the range of 1 to 10;

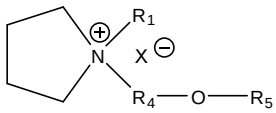
R_1, R_2, R_3, are, independently, hydrogen or alkyl substituents having 12 or fewer carbon atoms; and

R_6, R_7 and R_8 are, independently, hydrogen or alkyl substituents having 12 or fewer carbon atoms.

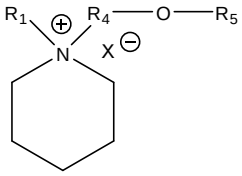
7. A zinc bromide electrolyte solution comprising one or more class A quat halides and one or more class B quat halides, each class A quat halide having a molecular structure selected from the group consisting of:



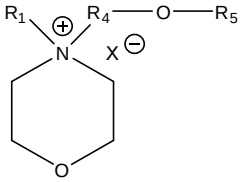
I



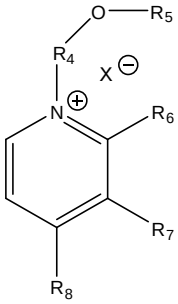
II



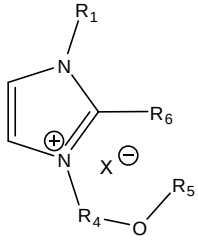
III



IV

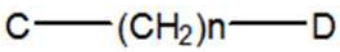


V

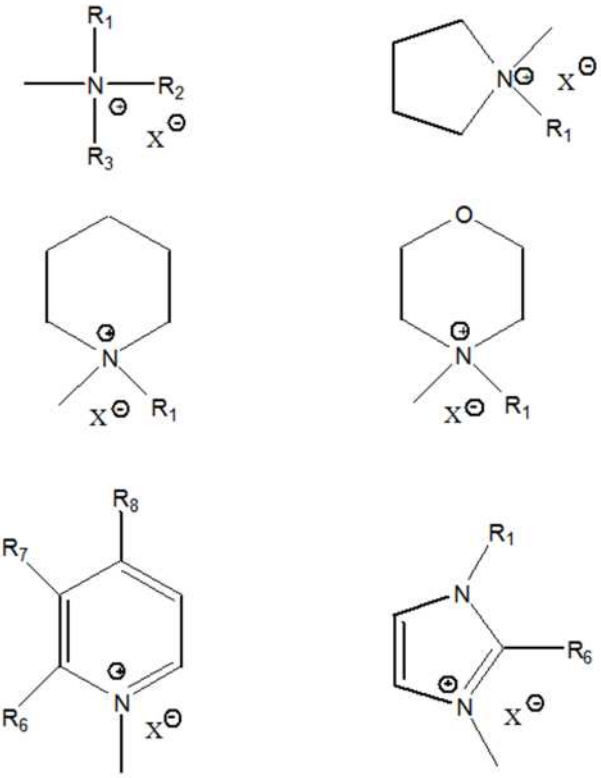


VI

and each class B quat halide having the following structure:



wherein C and D each are each independently selected from the group consisting of:



wherein

X^- is Br^- or Cl^-, or the quat is a mixture of both bromides and chlorides;

n is in the range of 1 to 10;

R_1, R_2, R_3, are, independently, hydrogen or alkyl substituents having 12 or fewer carbon atoms;

R_4 is an alkyl chain having in the range of 1 to 10 carbon atoms;

R_5 is an alkyl group having in the range of 1 to 6 carbon atoms; and

R_6, R_7 and R_8 are, independently, hydrogen or alkyl substituents having 12 or fewer carbon atoms.

8. An electrolyte solution as in claim 6 wherein the one or more class B quats is/are dimethylethyl gemini quat bromide with butyl linkage having the following structure:

