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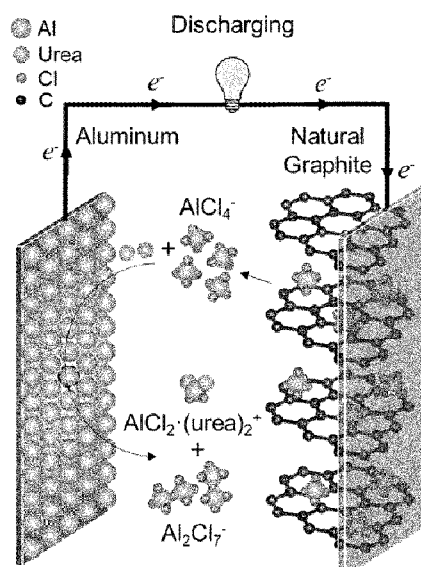
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FIGURE 1



(57) Abstract: Here is described an aluminum-ion battery technology having an electrolyte comprising an affordable aluminum trichloride (AlCl_3)/amide-based deep eutectic solvent, aluminum metal as the anode, and a compatible cathode material, preferably a graphitic material (pristine pyrolytic/natural graphite, treated pyrolytic/natural graphite (through heat-treatment for pyrolytic graphite; ultrasonication and microwave exfoliation for natural graphite)), an oxide or a sulfide-containing compound. A wide variety of applications ranging from energy storage in consumer electronics to electric vehicles to grid storage is considered.

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ALUMINUM-ION BATTERY USING ALUMINUM CHLORIDE/AMIDE-BASED DEEP EUTECTIC SOLVENTS

RELATED APPLICATION

This application claims priority under applicable law to United States provisional application No. 62/733,223 filed on September 19, 2018, the content of which is incorporated herein by reference in its entirety for all purposes.

TECHNICAL FIELD

The present technology relates to batteries, and more specifically, to Al-ion electrochemical cells using aluminum trichloride/amide-based deep eutectic solvents as the electrolyte, aluminum metal as anode, and compatible materials as cathode. The application also further relates to Al-ion batteries containing the electrochemical cells and to their uses.

BACKGROUND

Lead-acid batteries are well known examples of rechargeable electrochemical devices. With a history of more than 155 years, they are still widely used in various applications ranging from telecommunication to transportation. Lithium ion batteries have brought a paradigm shift to the electrochemical storage systems by outperforming lead-acid batteries in several areas, such as energy density, cycle life, efficiency, and maintenance. Despite impressive commercial penetration in the last 25 years and being a frontrunner among a variety of rechargeable batteries, the future of Li-ion batteries is debatable. The excessive consumption of Li and Co-based natural resources as a result of a significant increase in demand for Li-ion batteries, governed by the lifestyle of modern society together with dwindling and geographically restricted abundance of these natural resources, is a critical factor in sustaining cost-effective Li-ion batteries in the future. Considering a possible future shortfall of these resources, research studies and discussions at both academic and industry levels are endeavoring to find an alternative and sustainable battery chemistry using more earth-abundant materials than lithium.

Considering that aluminum is the third most abundant element in the Earth's crust and with the available fundamental knowledge of the electrochemistry of aluminum, the potential of aluminum cannot go unnoticed in the field of battery electrochemistry. There are two main factors that motivate research interest in aluminum-batteries. The first is inertness and ease of handling of Al in an ambient environment, which could provide a significant improvement in the safety of

aluminum-based batteries. The second factor relates to the high volumetric capacity of aluminum compared with Li, Na, K, Mg, Ca and Zn because of its ability to exchange three electrons and its relatively high density (2.7 g/cm^3 at 25°C), which could reduce the size of aluminum batteries. Aluminum also has higher gravimetric capacity compared with Na, K, Mg, Ca and Zn. Even with the higher redox potential of Al (1.76V vs. standard hydrogen electrode), with higher volumetric and gravimetric capacities, aluminum batteries could have close to or higher energy density compared with other metals. Furthermore, the low cost of aluminum could make aluminum-batteries much more economically feasible and could facilitate easier penetration into the market.

Despite the numerous advantages of aluminum-batteries, research efforts over the past 30 years have encountered several challenges, including low charge/discharge capacity; low discharge voltage (0.55V); short life cycle; cathode material disintegration; and a significant drop in efficiency over just a few cycles. More recently, Al-ion batteries have shown a well-defined voltage plateau, high coulombic efficiency, and reasonable capacity over a large number of cycles using an aluminum chloride (AlCl_3)/1-ethyl-3-methylimidazolium Chloride [EMIm]Cl ionic liquid electrolyte. Even though the performance of Al-ion batteries significantly improved with the utilization of ionic liquid electrolytes, the use of expensive [EMIm]Cl raised a concern with regards to the cost of the Al-ion batteries. Thus, reduction in the cost of Al-ion batteries is still a major barrier to its commercialization as large-scale energy storage devices. Other drawbacks include the evolution of toxic Cl_2 gas due to oxidation of AlCl_4^- (i.e., $4\text{AlCl}_4^- + 2\text{e}^- \rightarrow 2\text{Al}_2\text{Cl}_7^- + \text{Cl}_2$), and the corrosivity of these electrolytes, which limits the use of stainless steel as current collectors and cell packaging materials.

It would be advantageous to provide an aluminum-based battery which could deliver good performance while being relatively inexpensive to manufacture, and preferably having reduced toxicity and corrosivity.

SUMMARY

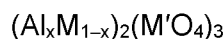
In a first aspect, the present technology relates to an electrochemical cell comprising an electrolyte, an anode and a cathode, wherein the electrolyte comprises AlCl_3 and an amide-based compound, and wherein the anode comprises metallic aluminum, for instance, wherein AlCl_3 and amide-based compound together form a deep eutectic solvent.

According to one embodiment, the amide-based compound is of formula $\text{R}^1\text{C}(\text{O})\text{R}^2$, wherein R^1 is NH_2 or $\text{C}_{1-6}\text{alkylNH}$ and R^2 is NH_2 , $\text{NHC}_{1-6}\text{alkyl}$ or $\text{C}_{1-6}\text{alkyl}$. For instance, R^1 and R^2 are each

NH₂ or NHC₁₋₃alkyl, or R¹ and R² are each NHC₁₋₃alkyl, or R¹ is NH₂ or C₁₋₃alkylNH and R² is C₁₋₃alkyl. In preferred embodiments, the amide-based compound is urea (*i.e.* wherein R¹ and R² are each NH₂), or the amide-based compound is *N,N'*-dimethylurea, or the amide-based compound is acetamide. In another embodiment, the electrolyte further comprises a co-solvent, e.g. 1,2-dichloroethane.

According to a further embodiment, the cathode comprises an electrochemically active material selected from:

- graphite;
- CuS, Ni₃S₂, Mo₆S₈, MoS₂, SeS₂, polypyrrene, zeolite-templated carbon and vanadium oxide; and
- a spinel oxide of the formula:



wherein:

M represents M₂^aM₃^bM₄^c, wherein:

M₂ is a bivalent metal element selected from the group consisting of Mg, Ca, Sr and Ba;

M₃ is a trivalent metal element selected from the group consisting of Sc, Y, Ga and In; and

M₄ is a tetravalent metal element selected from the group consisting of Zr and Hf;

M' is a hexavalent metal element; and

a, b, c and x are such that $0 \leq a < 1$, $0 \leq b < 1$, $c = a$, and $0 \leq x < 1$, wherein:

$$(2a/(1-x) + 3b/(1-x) + 4c/(1-x)) = 3.$$

In one embodiment, the cathode electrochemically active material comprises graphite. In some embodiment, the graphite comprises pyrolytic, natural or exfoliated graphite. For instance, pyrolytic graphite is pristine or the pyrolytic graphite is heat-treated, the natural graphite is pristine or the natural graphite is ultrasonicated. Alternatively, the exfoliated graphite is sonicated microwave-exfoliated graphite. In one embodiment, the cathode comprises sonicated microwave-exfoliated graphite as electrochemically active material and is a free-standing cathode.

In another embodiment, the cathode electrochemically active material comprises a vanadium oxide selected from VO_2 or V_2O_5 , preferably V_2O_5 . In a further embodiment, the cathode electrochemically active material comprises MoS_2 . In yet another embodiment, the cathode electrochemically active material comprises SeS_2 . In a further embodiment, the cathode electrochemically active material comprises the spinel oxide of the formula $(\text{Al}_x\text{M}_{1-x})_2(\text{M}'\text{O}_4)_3$, wherein x, M and M' are as herein defined, e.g. M' is W or Mo. In any of the embodiments of the present paragraph, the cathode may further comprise a conductive carbon.

In any of the above embodiments pertaining to the cathode, said cathode may further comprise a binder mixed together with the electrochemically active material.

According to another aspect, the present technology relates to a battery comprising at least one electrochemical cell as defined herein. For instance, the battery is an aluminum-ion battery. In one embodiment, the battery is for use in supplying electric power to a consumer electronic device. In another embodiment, the battery is for use in supplying electric power to a hybrid or electric vehicle. In a further embodiment, the battery is for use in storing electrical energy within an electrical power grid.

According to a further aspect, the present technology relates to a method of supplying electric power to an external device comprising:

- (a) providing an electrochemical cell as defined herein;
- (b) connecting the electrochemical cell to the external device; and
- (c) allowing the electric current to flow from the electrochemical cell to the external device.

In one embodiment of the above method, the electrochemical cell is a component of a battery. In another embodiment, the an external device is a consumer electronic device. In a further embodiment, the an external device is a hybrid or electric vehicle. In yet another embodiment, the electrochemical cell is a component of a battery used in storing electrical energy within an electrical power grid, and the device is connected to the electrical power grid.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic diagram of the reaction mechanism in AlCl_3 /urea deep eutectic solvent (DES) during discharge in a preferred embodiment of the present technology.

Figure 2 presents in (a) the Raman spectra of AlCl_3 /urea with molar ratios between 1.0 and 1.5 (a) 1.5 and in (b) the estimated relative concentrations of electroactive ionic species across various AlCl_3 /urea molar ratio.

Figure 3 shows in (a) the Arrhenius plot of conductivity vs $1000/T$ of binary AlCl_3 -urea DES and AlCl_3 -urea DES with co-solvents, and in (b) the comparison of conductivity of pure AlCl_3 -urea DES and with co-solvents at 25°C (● DCE; ▲ toluene).

Figure 4 illustrates cyclic voltammograms of: (a) aluminum (0.5 mV/s) and pristine pyrolytic graphite (1 mV/s); and (b) pristine natural graphite, sonicated graphite (30 and 60 min) and molybdenum at a scan rate of 1 mV/s with an AlCl_3 /Urea = 1.3 molar ratio electrolyte.

Figure 5 illustrates (a) the effect of temperature (red: 850°C ; black: 900°C) on the loading of heat-treated pyrolytic graphite sheet across different treatment time; and SEM images of: (a) pristine, (b) $900^\circ\text{C}/1\text{h}$ -treated, (c) $900^\circ\text{C}/2\text{h}$ -treated, and (d) $900^\circ\text{C}/3\text{h}$ -treated pyrolytic graphite.

Figure 6 presents in (a) the galvanostatic charge/discharge curves of pristine and $900^\circ\text{C}/2\text{h}$ -treated pyrolytic graphite sheet using AlCl_3 /urea = 1.3 electrolyte (2nd cycle); and (b) a stability test for pristine and $900^\circ\text{C}/2\text{h}$ -treated pyrolytic graphite sheets up to 20 cycles (specific charge/discharge current 10 mA/g (pristine pyrolytic graphite sheet), 25 mA/g ($900^\circ\text{C}/2\text{h}$ -treated pyrolytic graphite sheet); and 2.2V/1.0V upper/lower cutoff voltage).

Figure 7 shows schematic diagrams of AlCl_4^- intercalation mechanism into: (a) pristine pyrolytic graphite; and (b) heat-treated pyrolytic graphite.

Figure 8 provides SEM images of: (a) pristine, (b) 10 min, (c) 20 min, (d) 30 min, (e) 40 min, (f) 50 min, and (g) 60 min sonicated natural graphite; and the corresponding (h) particle size distribution; (i) Raman spectra and; (j) intensity ratio of D band over G band and estimated average domain sizes of pristine and sonicated natural graphite (natural graphite used: -10 mesh).

Figure 9 presents (a) the specific discharge capacity at different current densities of electrochemical cells using pristine (-10 mesh), 30-min sonicated, and 60-min sonicated natural graphite (loading $\sim 1.5 \text{ mg/cm}^2$), (b) its corresponding coulombic efficiency; (c) specific discharge capacity at different current densities of electrochemical cells using 30-min sonicated natural graphite with different loadings; and (d) its corresponding coulombic efficiency.

Figure 10 presents in (a) the long-term stability test of Al/30-min sonicated NG (1.0 mg/cm^2) up to 1000 cycles at a specific charge/discharge current at 100 mA/g for 20 cycles followed by charging-discharging at 600 mA/g; and in (b) the charge and discharge curves of the cell at the 100th, 200th, and 1000th cycles.

Figure 11 illustrates (a) a picture of microwave-exfoliated graphite (MWEG); (b) a picture of a free-standing sonicated MWEG attached to a molybdenum current collector using carbon conductive tape; and (c) the capacity retention at different current densities (scale bar: 1cm) for a MWEG cathode containing cell.

Figure 12 presents (a) comparisons of the cyclic voltammograms of molybdenum electrode in $\text{AlCl}_3/\text{urea} = 1.3$ (molar ratio) with different amounts of 1,2-dichloroethane addition (scan rate: 1 mV/s); (b) a stability test for Al/30-min sonicated NG (1.4 mg/cm^2) up to 200 cycles at a specific charge/discharge current at 100 mA/g for 10 cycles followed by charging-discharging at 600 mA/g using a 5% (v/v) DCE addition in the same deep eutectic solvent.

Figure 13 shows that discharge voltage profiles for (a) MoS_2 (loading: $\sim 1.2 \text{ mg/cm}^2$), (b) V_2O_5 ($\sim 1.0 \text{ mg/cm}^2$), and (c) SeS_2 ($\sim 1.5 \text{ mg/cm}^2$) across various cycles, using an $\text{AlCl}_3/\text{urea}=1.3$ (by mole) electrolyte.

DETAILED DESCRIPTION

All technical and scientific terms and expressions used herein have the same definitions as those commonly understood by the person skilled in the art relating to the present technology. The definition of some terms and expressions used herein is nevertheless provided below for clarity purposes.

When the term “approximately” or its equivalent term “about” are used herein, it means *approximately* or *in the region of*, and *around*. When the terms “approximately” or “about” are used in relation to a numerical value, it modifies it; for example, it could mean above and below its nominal value by a variation of 10%. This term may also take into account the probability of random errors in experimental measurements or rounding.

The expression “aluminum chloride/amide compound-based deep eutectic solvent” or similar expressions as used herein defines a class of ionic liquids composed of two components, their combination achieving a melting point which is much lower than that of its individual components.

More specifically, the deep eutectic solvent herein is the result of a combination of aluminum chloride (AlCl_3) and an amide-based compound.

The expression “amide-based” compound as used herein designates a class of compounds including small molecules comprising a urea or amide functional group, *i.e.* a carbonyl respectively between two nitrogen atoms or between nitrogen and carbon atoms. The nitrogen may be further substituted with an alkyl group while the carbon atom of the amide functional group is an alkyl group.

The term “alkyl” as used herein refers to saturated hydrocarbons having from one to six carbon atoms, including linear or branched alkyl groups. Examples of alkyl groups include, without limitation, methyl, ethyl, propyl, and isopropyl.

To at least partially overcome the challenges associated with prior art batteries, the inventors have adopted the use of a new class of ionic liquids, also known as deep eutectic solvents (DESs), as the electrolyte in the battery of the present technology. DESs have been selected in part because of their low cost and comparable physical and chemical properties to the relatively expensive $[\text{EMIm}]\text{Cl}$ materials. The reversibility of aluminum electrochemistry observed by the inventors in AlCl_3 /amide-based DES system offers an exciting possibility of low-cost electrolyte for rechargeable Al-ion batteries with minimal environmental footprint. To address stringent cost requirements of energy storage devices, the inventors have also focused in some examples on inexpensive, easily available graphitic materials (pyrolytic graphite and natural graphite flakes) that are being produced at industrial scales. Other cathode materials were nonetheless also tested. Moreover, by considering commercialization of the batteries in near future, several scalable processing methods of the pristine materials were utilized, and preliminary results showed superior battery performance in cyclability, specific capacity and rate capability/stability over known systems.

Following material selection, a series of electrochemical cells were produced using aluminum metal as the anode, graphitic materials as the cathode, and AlCl_3 /amide-based DESs as the electrolyte. For pyrolytic graphite-based cathode, heat treatment was found to be extremely effective in improving the electrochemical cell's specific capacity and rate capability, from 40 mAh/g (at 10 mA/g) to 55 mAh/g (at 25 mA/g). To date, the inventors are the first to report the positive effects of heat treatment of pyrolytic graphite, at the same time achieving this capacity in the Al/pyrolytic graphite/ AlCl_3 -amide-based system. For natural graphite-based cathodes,

electrochemical cells were prepared using pristine natural graphite flakes of different sizes, and also fragmented large natural graphite flakes (-10 mesh) into smaller particles through a simple ultrasonication approach. In addition to graphitic materials, the performance of other sulfide/oxide materials including MoS_2 , V_2O_5 , and SeS_2 were also investigated in Al batteries utilizing AlCl_3 -urea DESs.

The followings are some of the major outcomes observed in these experiments: (1) the performance of the batteries was significantly affected by the size of natural graphite flakes used, with a smaller size resulting in a higher specific capacity and rate capability; (2) ultrasonication greatly improved the specific capacity as well as rate capability of the batteries, where a significant improvement of specific capacity, from 35 (pristine natural graphite, -10 mesh) to 70 mAh/g (30- and 60-min sonicated natural graphite) was recorded; (3) by reducing the loading of 30-min sonicated natural graphite from 4.2 to 1.6 mg/cm, the specific capacity remarkably increased from ~20 to ~60 mAh/g at 200 mA/g, where appreciable specific capacities of ~45, ~25, and 10 mAh/g even at very high rates of 400, 800, and 1600 mA/g, respectively, were obtained; (4) addition of a co-solvent (1,2-dichloroethane, DCE) profoundly improved the ionic conductivity of the electrolyte (three-fold improvement with 20 wt% addition across all AlCl_3 /urea molar ratio), leading to enhanced specific capacity at higher charge/discharge rate; and (5) an Al/ AlCl_3 -urea/ SeS_2 system tested exhibited the highest average discharge voltage of ~1.5 V as compared to the existing literature on non-aqueous Al batteries utilizing oxide/sulfide cathodes.

Without wishing to be bound by theory, the following discusses the theoretical aspects behind our approach in developing this new generation of Al-ion batteries.

Desired features of room-temperature ionic liquids (RTILs), such as a wide electrochemical stability window, low vapor pressure, and reasonably high electrochemical conductivity, are very promising in the development of new energy storage devices with high capacity. Among them, RTILs formed by a combination of aluminum chloride (AlCl_3) with dialkylimidazolium chloride have been considered as the most promising candidates for Al-based batteries. By varying the molar ratio of AlCl_3 to dialkylimidazolium chloride (X_{AlCl_3}), intrinsic properties such as Lewis acidity/basicity, types of ionic species present, melting point, conductivity and electrochemical stability window of the electrolytes can be modulated. In Lewis basic melt where $X_{\text{AlCl}_3} < 0.5$, the ionic species present are Cl^- (in excess) and AlCl_4^- , while in Lewis acidic melt where $X_{\text{AlCl}_3} > 0.5$, several species such as AlCl_4^- , Al_2Cl_7^- , $\text{Al}_3\text{Cl}_{10}$, $\text{Al}_4\text{Cl}_{13}^-$ can form depending on X_{AlCl_3} . At a composition of $X_{\text{AlCl}_3} = 0.5$, such melt is called neutral melt and only AlCl_4^- is present. Since AlCl_4^-

ions cannot be reduced within the potential range in most applications, electrodeposition of aluminum is possible only in acidic melts following the equation:



When graphitic materials are used as the active materials in the cathode of an Al-based electrochemical cell, intercalation of AlCl_4^- in between graphene layers during charging occurs:



Hence, the overall redox reaction in a typical Al/graphite cell using Lewis acidic AlCl_3 -dialkylimidazolium chloride electrolyte follows:

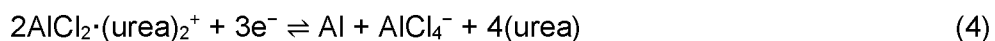


However, the use of expensive [EMIm]Cl raised significant cost issues, which hindered the large-scale commercialization and industrialization of Al-ion batteries.

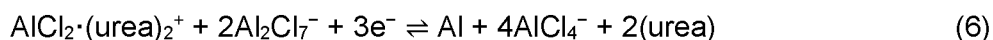
The different approach as described herein is based on using an affordable, nontoxic electrolyte by combining AlCl_3 with an amide-based compound (*i.e.* an amide or urea compound), and more specifically of urea which is a widely available commercial fertilizer.

Previous studies on the electrodeposition of aluminum in AlCl_3 -amide (both urea and acetamide) at room temperature suggested that the deposition of aluminum in neutral AlCl_3 /urea melt (AlCl_3 /urea = 1 by mole) was predominantly through the reduction of $\text{AlCl}_2 \cdot (\text{amide})_n^+$ species because AlCl_4^- cannot be reduced within the potential window. Another recent study further referred to the presence of cationic $\text{AlCl}_2 \cdot (\text{urea})_2^+$ in a neutral AlCl_3 /urea melt, where an electrochemical cell that operated at room temperature for 200 cycles using acidic AlCl_3 -urea electrolyte that contained $\text{AlCl}_2 \cdot (\text{urea})_2^+$, AlCl_4^- and Al_2Cl_7^- was also reported.

These previous studies further suggested that in AlCl_3 /urea ≥ 1.0 (molar ratio), the electrodeposition/stripping of aluminum would likely be dominated by $\text{AlCl}_2 \cdot (\text{urea})_n^+$ and subsequently by Al_2Cl_7^- through the following pathways:

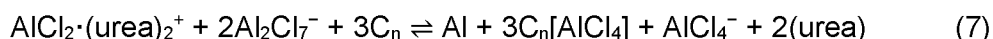


However, experimental results described herein indicate that appreciable electrochemical activity is observed only in the acidic melt (for instance, $\text{AlCl}_3/\text{urea} = 1.1$ by mole) but not in the neutral melt ($\text{AlCl}_3/\text{urea} = 1.0$). Combining these findings with the results previously reported, here is proposed that the electrodeposition/stripping of Al at the anode in acidic $\text{AlCl}_3/\text{urea}$ melts follows the mechanism below:



Essentially, Equation 6 combines Equations 4 and 5 by taking both electroactive cationic and anionic species ($\text{AlCl}_2 \cdot (\text{urea})_2^+$ and Al_2Cl_7^-) into consideration.

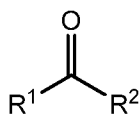
On the other end, when graphite materials are used as the cathode material, intercalation reaction at the cathode is considered to be the same as mentioned in Equation 3, where the dominant overall redox reaction in an Al/graphite cell using Lewis acidic AlCl_3 -acidic electrolyte would be as follows:



A schematic diagram of the reaction mechanism in an Al/graphite cell using acidic $\text{AlCl}_3/\text{urea}$ electrolytes during discharge is illustrated in Figure 1.

Accordingly, the present technology relates to an aluminum-ion electrochemical cell comprising an electrolyte between an anode and a cathode, where the electrolyte comprises AlCl_3 and an amide-based compound as defined herein, and wherein the anode comprises metallic aluminum. The electrochemical cell optionally further comprises a separator between the anode and cathode, in which the electrolyte is impregnated. For instance, the AlCl_3 and amide-based compound form a deep eutectic solvent.

The amide-based compound may be further defined by the formula $\text{R}^1\text{C}(\text{O})\text{R}^2$, also illustrated as follows:



wherein:

R^1 is NH_2 or $\text{C}_{1-6}\text{alkylNH}$; and

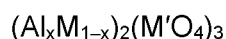
R^2 is NH_2 , $\text{NHC}_{1-6}\text{alkyl}$ or $\text{C}_{1-6}\text{alkyl}$.

For instance, the compound is an amide and R^1 is NH_2 or $C_{1-3}alkylNH$ and R^2 is $C_{1-3}alkyl$, such as acetamide. In other examples, the compound is a urea and R^1 and R^2 are each NH_2 or $NHC_{1-3}alkyl$, for instance, R^1 and R^2 being each $NHC_{1-3}alkyl$, such as *N,N'*-dimethylurea. Preferably, R^1 and R^2 are each NH_2 .

Some examples of deep eutectic solvents presented herein further comprise a co-solvent, wherein this co-solvent is inert in the presence of the other components of the battery. For instance, the co-solvent is a chlorinated aliphatic solvent such as 1,2-dichloroethane. The concentration of co-solvent is within the range from 1% to 30%, from 1% to 20%, or from 2% to 15%, or from 5% to 10%, or of 5% or less, or from 1% to 5%, all by volume in the total volume of electrolyte. In examples where the cathode material is of graphitic nature, then the concentration of co-solvent may be of 5% or less, or within the range from 1% to 5%, or from 2% to 5%, or from 1% to 4%, by volume in the total volume of electrolyte. In examples where the cathode material is of non-graphitic nature (e.g. sulfides or oxides), then the concentration of co-solvent is within the range from 1% to 30%, from 1% to 20%, or from 2% to 15%, or from 5% to 10%, all percentages expressed by volume in the total volume of electrolyte.

In this electrochemical cell, the cathode comprises a cathode active material electrochemically compatible with aluminum as the anode active material. More specifically the cathode comprises an electrochemically active material selected from:

- graphite;
- CuS , Ni_3S_2 , Mo_6S_8 , MoS_2 , SeS_2 , polypyrrene, zeolite-templated carbon and vanadium oxide; and
- a spinel oxide of the formula:



wherein:

M represents $M_2^aM_3^bM_4^c$, wherein:

M_2 is a bivalent metal element selected from the group consisting of Mg, Ca, Sr and Ba;

M_3 is a trivalent metal element selected from the group consisting of Sc, Y, Ga and In; and

M_4 is a tetravalent metal element selected from the group consisting of Zr and Hf;

M' is a hexavalent metal element; and

a, b, c and x are such that $0 \leq a < 1$, $0 \leq b < 1$, $c = a$, and $0 \leq x < 1$, wherein:

$$(2a/(1-x) + 3b/(1-x) + 4c/(1-x)) = 3.$$

For instance, the electrochemically active cathode material comprises a graphite which may be pyrolytic, natural or exfoliated graphite. One example includes pyrolytic graphite which is pristine or heat-treated. Another example is natural graphite, which can be natural or ultrasonicated. Preferably, the graphite is a sonicated or heat-treated graphite. A further example of a cathode active material is sonicated microwave-exfoliated graphite. For instance, the cathode comprises sonicated microwave-exfoliated graphite as electrochemically active material and the cathode is a free-standing cathode.

Examples of vanadium oxide as electrochemically active material include VO_2 and V_2O_5 , preferably V_2O_5 . Other electrochemically active materials of interest are MoS_2 and SeS_2 . When the electrochemically active material comprises the spinel oxide of formula $(\text{Al}_x\text{M}_{1-x})_2(\text{M}'\text{O}_4)_3$ as defined herein, then M' may be or comprise W or Mo.

The cathode material as defined herein may further comprise, in addition to the electrochemically active material, a conductive carbon and/or a binder.

A battery is also contemplated, where such battery comprises at least one electrochemical cell as defined herein, wherein said battery is an aluminum-ion battery. The battery surpasses the state-of-the-art in terms of cyclability, maximum specific capacities, and rate capabilities. Because the components used in this novel Al-ion battery are inexpensive, non-hazardous and widely available, large-scale production and application become economically viable.

The present batteries and electrochemical cells may be used in any method or device requiring electric power storage and/or supply. General uses include supplying electric power to a consumer electronic device or to a hybrid or electric vehicle or storing electrical energy within an electrical power grid, e.g. large-scale grid storage.

A method of supplying electric power to an external using the present electrochemical cells comprises:

- (a) providing an electrochemical cell as defined according to any of the aforementioned embodiments;

- (b) connecting the electrochemical cell to the external device; and
- (c) allowing the electric current to flow from the electrochemical cell to the external device.

For instance, the electrochemical cell is a component of a battery. In some examples of this method, the external device is a consumer electronic device or a hybrid or electric vehicle. Alternatively, the battery is used in storing electrical energy within an electrical power grid, and the device is connected to the electrical power grid.

When used in consumer electronics, the present aluminum-ion batteries could address potential safety issues (fire/explosion hazard) associated with lithium-ion batteries. The non-hazardous nature of the components used in the present technology ensures overall ease of handling during application as well as transportation. In addition, the economic aspects of the battery that utilizes widely available components (aluminum, graphite, and urea) could significantly lower production costs.

Like most ionic liquids and deep eutectic solvents, AlCl_3 /urea electrolyte exists as liquid across a wide range of temperatures. Accompanied by the low partial pressure of the electrolyte, hybrid/electric vehicles that utilize the present aluminum-ion batteries could potentially handle extreme weather conditions. Similarly, with the implementation of this battery technology, a marked production cost reduction is expected over conventional Li-ion and nickel-metal hydride batteries.

The use of the present batteries in grid energy storage, the components used in these batteries do not pose geographical limitations as opposed to current energy storage that uses Li-based materials. The present batteries ensure a lower cost, safety, reliability, and materials abundance. In addition, the theoretical energy density for Al-ion batteries (1060 Wh/kg) is higher than of lithium-ions (406 Wh/kg). A higher capacity is theoretically attainable through appropriate engineering of the cathode materials.

EXAMPLES

The following non-limiting examples are illustrative embodiments and should not be construed as further limiting the scope of the present invention. These examples will be better understood with reference to the accompanying figures.

Example 1: Materials and equipment*(a) Materials*

Anhydrous aluminum chloride (99.985 %), aluminum shots (99.999 %), molecular sieves (3A, 1-2 mm), N-methyl-2-pyrrolidinone (NMP, $\geq 99\%$), Super P™ conductive carbon black ($\geq 99\%$), and natural graphite flakes with different grain sizes: -10 mesh (99.9 %), -325 mesh (99.8 %), and median size 7-10 μm (99 %) were supplied by Alfa Aesar (USA). Aluminum foil (thickness: 50 μm , 99.999 %) and molybdenum sheet (thickness: 130 μm , 99.95 %) were purchased from Beijing Loyaltarget Tech. Co., Ltd. (China). Vanadium (V) oxide ($\geq 99.6\%$), molybdenum (IV) sulfide powder (98 %, < 2 μm), selenium sulfide (SeS_2), polyvinylidene fluoride (PVDF, M_w : ~534000) and glass microfiber separators (GF/A and GF/F, Whatman) were obtained from Sigma-Aldrich Co. (USA). 1,2-dichloroethane (DCE) and toluene were obtained from Caledon Laboratory Ltd and Anachemia, respectively. Pyrolytic graphite sheet (thickness: 25 μm) was purchased from Panasonic (Japan). Urea ($\geq 99.5\%$) and sodium alginate were acquired from Bioshop Canada Inc (Canada) and Landor Trading Co. Ltd. (Canada), respectively.

In the preparation of electrochemical cells, several components such as carbon conductive tape (Electron Microscopy Sciences (USA)), quartz cuvette cells (1 ml, Purshee Optical Elements Co., Ltd. (China)) hot melt adhesive tape (Gelon LIB Co. Ltd. (China)), aluminum laminated film for pouch cell (TMAX Battery Equip. (China)) were used.

(b) Purification of raw materials

Prior to usage, as-received Al foil and Al shots were ultrasonicated in anhydrous ethanol for 5 mins to remove surface impurities. In removing intrinsic aluminum oxide layers, acidic etching using HNO_3 (8 M) was found to be more efficient than alkaline etching in NaOH (1.25 M). Here, Al foil and Al shots were dipped in 8 M HNO_3 for 5 min followed by washing with distilled water until pH reached ~7. Right after distilled water was removed, Al foil and Al shots were dipped in acetone before being placed inside the transfer chamber of a glovebox. Then, they were subjected to vacuum for over 15 min to remove any remaining liquid on the surface before being transferred to the main chamber.

Urea (or carbamide) was vacuum dried at 100°C for 24 hours and transferred to the glovebox immediately after discharging from the vacuum oven.

Prior to usage, DCE and toluene were soaked in molecular sieves for weeks to minimize the water content in the solvents.

(c) Drying of containers

Prior to usage, all containers and components (quartz cuvette cells, beakers, glass vials, magnetic stirrers, etc.) were vacuum dried at 80°C overnight and were immediately stored inside the glovebox.

Example 2: Preparation of deep eutectic solvents (DESs)

The AlCl_3 -amide-based (in this case urea) deep eutectic solvent (DES) was prepared by mixing urea and anhydrous AlCl_3 in varying molar ratios in a glass beaker under constant magnetic stirring in an argon-filled glove box (O_2 and H_2O < 1 ppm). For example, for an AlCl_3 /urea molar ratio of 1.3, 11.54 g of AlCl_3 is mixed with 4.00 g of urea. To prevent decomposition of the electrolyte, the mixing of AlCl_3 and urea was either performed under cryogenic conditions (ice-gel patches being used to regulate the mixture's temperature) or through slow addition of the AlCl_3 into urea. A transparent, yellowish, and viscous liquid was obtained after stirring the mixture overnight at ambient temperature. To remove impurities such as HCl (formed as a result of residual H_2O) and colored organic impurities in the electrolyte, Al shots were added, and the mixture was heated at 60°C for 30 minutes. Right after heating, the electrolyte was subjected to vacuum for five minutes in the transfer chamber of the glovebox to remove residual gases from the electrolyte. This heating-vacuum treatment procedure is repeated twice in total. Prior to usage, the electrolyte was again placed under vacuum for 15 minutes.

AlCl_3 -urea DESs (molar ratio: 1.1-1.5) with the addition of 20 wt.% of a co-solvent (DCE and toluene) were also prepared by slowly adding the designated co-solvent into the AlCl_3 -urea DES under constant magnetic stirring. Other electrolytes comprising 2.5%, 5% and 10% v/v of DCE were also prepared using the same procedure.

Example 3: Preparation of cathodes

(a) Pristine pyrolytic graphite sheet (Pristine PGS)

As-received pyrolytic graphite sheet (PGS) was subjected to repeated centrifugal treatment (4000 rpm/10 minutes/5 times) in deionized water before drying overnight under vacuum at 80°C. The

resulting PGS was herein named as Pristine PGS. The Pristine PGS was fixed to a molybdenum tab using carbon conductive tape to form a cathode.

(b) Heat-treated pyrolytic graphite sheet (Heat-treated PGS)

As-received PGSs were heat-treated at 850 and 900°C at varying residence time in alumina crucibles in a muffle furnace. The heat-treated pyrolytic graphite sheets (heat-treated PGS) were subjected to repeated centrifugal treatment (4000 rpm/10 minutes/5 times) in deionized water before drying overnight under vacuum at 80°C. The weight of heat-treated PGS was determined immediately after withdrawing from the vacuum furnace and the area was determined using free software (ImageJ™). The obtained weight and apparent area were used to determine the loading of heat-treated PGS under different temperatures and heat treatment time. The Heat-treated PGS thus obtained was fixed to a molybdenum tab (Mo tab) using carbon conductive tape to form a cathode.

(c) Pristine natural graphite (Pristine NG)

The binder for natural graphite was prepared by mixing 15ml of distilled water with 0.3g of sodium alginate in a 20-ml glass vial and the resulting mixture was magnetically stirred overnight at room temperature until a homogeneous viscous mixture was obtained.

In the context of this disclosure, natural graphite flakes (-10 mesh, -325 mesh and median size 7-10 µm) that were used as-received are referred to as pristine natural graphite (Pristine NG). The graphite slurry was prepared by stirring 950 mg of Pristine NG and 2.5 ml of sodium alginate binder overnight to yield a viscous slurry. The resulting slurry was doctor-bladed onto a piece of Mo tab (current collector) of which the mass was predetermined. Scotch tape was utilized to limit the surface area of the graphite slurry coating. The resulting Mo tab was vacuum dried at around 50°C for a few hours. Upon withdrawal from the vacuum furnace, the scotch tape was detached from the Mo tab and acetone was used to remove remaining adhesive on the surface of the Mo tab. To evaluate the loading of graphite slurries, the cathode was heated again at 80°C overnight and the heated cathode was immediately weighed after withdrawing from the vacuum furnace. The area of the graphite slurry was determined using ImageJ™.

(d) Sonicated natural graphite (Sonicated NG)

Pristine natural graphite flakes (-10 mesh, 1g) were placed into a 50-ml test tube filled with 20 ml of anhydrous ethanol and sonicated for 10-60 min at a 10-min step using Misonix ultrasonic liquid

processor (XL-2000 series) operated at a power output wattage of 15. During ultrasonication, the test tube was immersed in an ice bath to prevent heat-up of the suspension. The resulting suspension was centrifuged for 1 hour at 4000 rpm to isolate graphite particles from ethanol. With the help of a pipette, ethanol was carefully taken out and the remaining solid was dried under vacuum at 60°C overnight to afford Sonicated NG (sonicated for various durations).

The electrode was prepared with a sodium alginate binder on a Mo tab current collector as in Example 3(c) with the exception that the Pristine NG was replaced with the Sonicated NG.

(e) Free-standing sonicated microwave-exfoliated graphite (MWEG)

The preparation of free-standing sonicated microwave-exfoliated graphite (MWEG) involved several steps. Pristine natural graphite (1 g, -10 mesh) was first mixed with 5 ml of a concentrated sulfuric acid (98 wt. %)-hydrogen peroxide (30 wt. %) mixture (20:1 by volume) for 1 hour at room temperature followed by washing with distilled water until pH reached 4~5. After drying at 100°C for over 24 hours, expandable graphite (EG) was obtained. Then, microwave-exfoliated graphite (MWEG) was obtained by exfoliating 0.2g of EG under microwave irradiation, at a power of 960W for 40 seconds in a porcelain dish under N₂ environment. The resulting MWEG was washed again with distilled water until the pH reached 5~6 and subsequently dried overnight under vacuum at 100°C. In the preparation of free-standing sonicated MWEG electrode, approximately 0.2g of dried MWEG were dispersed in 20 ml of ethanol and the resulting suspension was ultrasonicated for 2h at a power output wattage of 15. The sonicated suspension was filtered through a PVDF membrane (0.22 µm pore size, Millipore). Subsequently, the sonicated MWEG (along with the membrane) was vacuum-dried at 60°C overnight. A free-standing felt with a loading of approximately 8mg/cm² was obtained by physical separation of the sonicated MWEG from the PVDF membrane. A cathode was finally prepared by shaping the free-standing sonicated MWEG into a dimension of 1×1 cm², and subsequently attached to a Mo current collector using carbon conductive tape.

(f) Molybdenum (IV) sulfide (MoS₂)

The V₂O₅ slurries was prepared by mixing 0.80 g of MoS₂, 0.10 g of Super P™ conductive carbon, and 0.10 g of PVDF (dissolved in NMP) overnight to yield a homogenous slurry. The electrode fabrication process followed the same procedure as Example 3(c) but using the present materials and amounts.

(g) Vanadium (V) oxide (V_2O_5)

The V_2O_5 electrode was prepared using the materials, amounts and procedure presented in Example 3(f) while replacing MoS_2 with V_2O_5 .

(h) Selenium sulfide (SeS_2)

SeS_2 slurries were prepared by mixing 0.75 g of SeS_2 , 0.10 g of Super P™ conductive carbon, and 0.15 g of PVDF (dissolved in NMP) overnight to yield a homogenous slurry. The electrode fabrication process followed the procedure detailed in Example 3(c) while using these materials.

Example 4: Preparation of electrochemical cells

(a) Quartz cuvette cells (Al / electrolyte / PGS)

Electrochemical cells were contained in quartz cuvette cells and were assembled in an argon-filled glove box. The specific charge/discharge currents (mA/g) and the specific capacities (mAh/g) herein are referred to the cathode (PG) mass. The anode (Al foil) and cathode (Examples 3(a) and 3(b)) were separated by a layer of glass microfiber separator (GF/F, Whatman) to prevent shorting. The partially assembled cell was dried overnight in a vacuum desiccator before transferring into the glovebox. The electrolyte (~750 μ l of $AlCl_3$ /Urea = 1.3 by mole) was injected and the cell was closed using a polytetrafluoroethylene (PTFE) cap. PTFE thread seal tape was utilized to further seal the current collectors/cuvette cell interface. Galvanostatic charge-discharge testing was conducted at 10 mA/g in the voltage range of 1.0 to 2.2 V using a potentiostat (VersaSTAT 3™, Princeton Applied Research).

(b) Pouch cells (Al / electrolyte / NG, MWE, MoS_2 , V_2O_5 , or SeS_2)

An as-prepared cathode of Examples 3(c), (d), (e), (f), (g) or (h) and a piece of glass fiber membrane (GF/A or GF/F) were placed inside a partially heat-sealed aluminum-laminated film pouch with two open ends. The partially fabricated pouch assembly was heated at 80°C overnight under vacuum and was swiftly transported to the glovebox right after heating. In the glovebox, a piece of Al-foil (acting as an anode as well as a current collector) was inserted into the pouch and the assembly was removed from the glovebox. The open end with current collectors was immediately heat-sealed and rapidly readmitted into the glovebox. During sealing, current collectors were sandwiched between hot melt adhesive that was utilized to improve the sealing at the current collector/pouch interface. Approximately 3 ml of electrolyte ($AlCl_3$ /urea = 1.3 by

mole) was injected using a glass Pasteur pipette. The cell was then removed from the glove box and the remaining open end was instantly heat-sealed. The specific charge/discharge currents (mA/g) and the specific capacities (mAh/g) herein are referred to relative to the mass of active materials.

Example 5: Characterization and electrochemical measurement methods

(a) Electrochemical performance

To determine the rate capability of Al/Pristine NG and Al/Sonicated NG cells, current densities ranging from 50 to 200 mA/g (step size: 25 mA/g, 20 cycles, charge/discharge cut-off voltage: 2.2/1.0 V) were used. For Al/MoS₂ and Al/V₂O₅ systems, the cells were cycled at a current density of 25 mA/g with charge and discharge cut-off voltage at 2.0 and 0.1 V, respectively. For Al/SeS₂ system, the cell was charged/discharged at 50 mA/g with charge and discharge cut-off voltage at 2.0 and 0.5 V, respectively. All galvanostatic tests were conducted using a multichannel battery tester (CT-4008, Neware).

(b) Cyclic voltammetry

Cyclic voltammetry (CV) measurements were carried out using a potentiostat in a three-electrode configuration. Al foil, pristine PGS, pristine NG, sonicated NG, and Mo tabs were used as the working electrodes in separate experiments. Al foil was used as both the auxiliary and the reference electrode in all experiments. The electrochemical cell was assembled in a quartz cuvette cell (1.75 ml) containing AlCl₃/Urea of 1.3 by mole in a glove box and was closed with a PTFE cap. The electrochemical cell was then sealed with PTFE thread seal tape. The scanning voltage range was set from -0.6 to 0.6 V (vs Al) for Al foil, 0.6 to 2.4 V (vs Al) for pristine PGS and 0.5 to 2.4 V (vs Al) for pristine NG, sonicated NG, and Mo tab. Except for Al foil for which a scan rate at 0.5 mV/s was used, the scan rate of pristine PGS, pristine NG, sonicated NG, and Mo tab was kept at 1.0 mV/s.

(c) Conductivity

The conductivity measurements for all DESs were obtained by employing electrochemical impedance spectroscopy (EIS) measurements using a potentiostat (VersaSTAT™ 3, Princeton Applied Research) at a perturbation amplitude of 10 mV in the frequency range. EIS measurements were performed in the range from 25 to 85 °C (± 1 °C) for binary AlCl₃-urea DESs, and in the range of 25 to 65 °C (± 1 °C) for AlCl₃-urea DESs with co-solvent additions. Each mixture

was contained in a well-sealed PTFE cell with Mo (3 mm-diameter) as the working and auxiliary electrodes. For each measurement, the DESs were let to equilibrate at each designated temperature in an Ar-filled oven for 12 h prior to conducting the measurement.

(d) Raman spectroscopy

DESs: One drop of the electrolytes ($\text{AlCl}_3/\text{Urea} = 1.3$ and 1.5 by mole) was transferred into a quartz cuvette cell (375 μl) using a glass Pasteur pipette. The spectrum of the electrolytes was acquired ($40\text{--}1540\text{ cm}^{-1}$) by a Dispersive Raman Microscope (Bruker) using Ar^+ laser (532 nm) at a resolution of 0.5 cm^{-1} .

NGs: Raman spectra of pristine and sonicated natural graphite (~ 10 mesh) were acquired using the same dispersive Raman microscope and under the same measurement conditions as mentioned.

(e) Scanning electron microscopy (SEM)

A scanning electron microscope (model SU3500, from Hitachi) was utilized to investigate the surface morphology of pristine pyrolytic graphite, heat-treated pyrolytic graphite, pristine natural graphite, and sonicated natural graphite, respectively as prepared in Examples 3(a) to 3(d).

(f) Particle size analysis

The effects of sonication time on the particle size distributions of sonicated natural graphite were investigated using a particle size distribution analyzer (Partica™ LA-950, from Horiba).

Example 6: Characterization and electrochemical measurement results

(a) Characterization of electrolytes (DESs)

In evaluating the relative concentrations of ionic species in $\text{AlCl}_3/\text{urea}$ DESs, Raman spectroscopy was performed as in Example 5(d), and the results are presented in Figure 2 (a). Raman spectroscopy revealed the presence of AlCl_4^- (314 cm^{-1}) and Al_2Cl_7^- (348 cm^{-1}) in the electrolytes used in this study. In addition, when the molar ratio of AlCl_3 to urea increased from 1.0 to 1.5, Al_2Cl_7^- peak at 314 cm^{-1} significantly intensified relative to that of AlCl_4^- , indicating an increase in Al_2Cl_7^- concentration at higher $\text{AlCl}_3/\text{urea}$ molar ratio. By combining the ratio of the Raman scattering cross-sections (K) between Al_2Cl_7^- and AlCl_4^- anions derived for the 1-butyl-3-methylimidazolium chloride/ AlCl_3 system ($K = 0.87$), the relative concentration of $\text{Al}_2\text{Cl}_7^-/\text{AlCl}_4^-$

was estimated to increase from 0.43 to 1.24 for $\text{AlCl}_3/\text{urea} = 1.1$ and 1.5, respectively (Figure 2(b)). In addition, by taking the charge neutrality of the system into consideration, it was estimated that the relative concentration of $\text{AlCl}_2^+(\text{urea})_n^+$ was higher than Al_2Cl_7^- across the acidic compositions evaluated.

Figure 3a demonstrates the behavior of the conductivity vs temperature for the investigated mixtures. The conductivities of AlCl_3 -urea DES were significantly enhanced by both DCE and toluene additions. For instance, the conductivities of AlCl_3 -urea DESs experienced a three-fold increase with an addition of 20 wt% of the co-solvents at 25°C. (Figure 3(b)). Generally, the temperature dependence of ionic conductivities $\sigma(T)$ of RTILs can be described by the Vogel-Fulcher-Tamman (VFT) equation:

$$\sigma(T) = \sigma_0 \exp\left(-\frac{E'_{im}}{k_B(T-T_g)}\right) \quad (8)$$

where σ_0 (mS/cm) is the pre-exponential constant, E'_{im} is the pseudo-activation energy for ion mobilization (meV), k_B is the Boltzmann constant (8.617×10^{-2} meV/K), T is the experimental temperature (K), and T_g is defined as the ideal glass transition temperature (K). The corresponding VFT best-fits parameters are given in Table 1.

Table 1. VFT Best-fits parameters for binary AlCl_3 -urea DESs and AlCl_3 -urea DESs with 20 wt% co-solvent additions.

$\text{AlCl}_3/\text{Urea}$ molar ratio	No addition				20wt.% DCE addition				20 wt.% toluene addition			
	σ_0 (mS/cm)	E'_{im} (meV)	T_g (K)	R^2	σ_0 (mS/cm)	E'_{im} (meV)	T_g (K)	R^2	σ_0 (mS/cm)	E'_{im} (meV)	T_g (K)	R^2
1.0	66.0	20.7	237.8	0.9986	—	—	—	—	—	—	—	—
1.1	80.6	25.1	231.0	0.9984	23.3	7.9	244.7	0.9949	52.7	20.1	210.0	0.9987
1.2	115.7	32.6	212.0	0.9995	24.1	8.7	243.9	0.9910	54.9	20.7	206.4	0.9983
1.3	135.5	35.7	206.2	0.9997	21.2	9.9	231.0	0.9958	51.7	19.9	208.3	0.9997
1.4	127.1	36.2	205.3	0.9977	18.6	8.3	235.6	0.9966	47.1	19.8	207.7	0.9994
1.5	105.5	34.0	208.2	0.9998	19.9	9.5	230.4	0.9981	40.6	19.8	200.4	0.9899

From the results, E'_{im} generally increased with increasing $\text{AlCl}_3/\text{urea}$ molar ratio, indicating a larger mobilization resistance experienced by ionic species present in the mixture as AlCl_3 content increased. Such a phenomenon may be explained through a combined contribution of increasing concentration of Al_2Cl_7^- at higher $\text{AlCl}_3/\text{urea}$ molar ratio and the larger size of Al_2Cl_7^- relative to AlCl_4^- . With relatively higher Al_2Cl_7^- concentration at higher AlCl_3 content, the mixture is expected to experience a larger overall resistance for mobilization as the concentration of larger size anions increases, resulting in an increase in E'_{im} at higher $\text{AlCl}_3/\text{urea}$ molar ratio. In addition, the E'_{im} for

AlCl₃-urea DESs with additions of co-solvents demonstrated significantly lower values as compared to non-added mixtures. This could be attributed to a decrease in viscosity of the mixture that facilitates ion mobilizations. On the other hand, T_g was found to decrease with increasing AlCl₃/urea molar ratio, suggesting a decrease in the ideal glass transition temperature as AlCl₃ content increased. Since T_g is defined as the temperature at which the fluidity of a mixture would decrease to zero, a decrease in T_g implies a smaller tendency of AlCl₃-urea DESs to undergo glass-transition as temperature decreases. Similar effects of increasing AlCl₃ content on E'_{im} and T_g were also reported in other RTILs.

(b) Cyclic voltammetry

Cyclic voltammetry was performed using the procedure detailed in Example 5(b). As can be seen in Figure 4(a), a well-defined graphite oxidation peak is observed in the range of 1.5-2.4 V, attributed to graphite oxidation through intercalation of anions in pristine pyrolytic graphite from Example 3(a). The gradient of the oxidation peak is low in the 1.5-1.9 V region and increases significantly after that. The reduction process of graphite through de-intercalation of anions starts at around 2.0 V and several reduction peaks are observed in the region of 1.8-1.3 V. In the case of Al, the major peak of Al reduction and oxidation was obtained at -0.6 to -0.1 V and -0.1 to 0.3 V, corresponding to Al electrodeposition/reduction and Al dissolution/oxidation during charging and discharging, respectively. Although the oxidation/reduction of Al was quite reversible, it took several cycles, until a stable oxidation curve was obtained, which could be due to unintended side reactions, such as a slow dissolution of the aluminum oxide layer.

As shown in Figure 4(b), all natural graphite-based electrodes (from Examples 3(c) and (d)) showed similar electrochemical behavior with oxidation appearing in the voltage region between 1.5 and 2.4 V, while reduction occurred between 0.7 and 2.15 V. Similar to the pyrolytic graphite-based electrode, these redox waves can be attributed to intercalation/de-intercalation of chloroaluminate ions in-between the graphite layers. It is noticeable that the current density of natural graphite-based electrodes is significantly higher than that of pyrolytic graphite, indicating faster redox kinetics in natural graphite-based electrodes. As for the voltammogram of molybdenum current collector, no electrochemical activity was observed in the range studied. This ensures the electrochemical stability of Mo in AlCl₃/urea electrolyte.

(c) PGS-based electrodes

Figure 5(a) presents the reduction in the loading of PGS electrodes prepared according to Examples 3(a) and (b) across various heating temperatures and times. As compared with 850°C, the reduction in the loading of PGS is observed to be significantly higher at 900°C across all treatment times; indicating the oxidation of PGS is more profound at higher temperature. In investigating the effect of heat treatment on the surface morphology of PGS, the SEM images of pristine and heat-treated PGS at 900°C for 1, 2, and 3 hours are shown in Figure 5(b)-(e), respectively. As heat treatment time increased, pit size and penetration depth became progressively larger and deeper, proceeding from the surface down to the bulk. Prolonged heat treatment resulted in the formation of large cavities with the layered structure as observed in Figure 5(e). This can be associated with the exponential increase in the oxidation rate of pyrolytic graphite above 700°C.

Figure 6(a) illustrates galvanostatic charge-discharge curves (2nd cycle) of Al/pristine PGS and Al/heat-treated PGS cells at a current density of 10 and 25 mA/g, respectively. Both electrochemical cells demonstrated two discharge voltage plateaus from 1.9-1.7 V and 1.6-1.4 V corresponding to the reduction peaks presented in the CV diagrams observed. These reasonably high discharge voltage plateaus are consistent with reported Al-ion charge-storage systems using AlCl_3 /urea DESs. By subjecting pristine PGS to heat treatment at 900°C for 2 h, a significant increase in specific capacity from 40 to 55 mAh/g (38 % increase) is observed at the second cycle. Such increase in capacity arising from heat treatment of PGS is unprecedented in Al-ion charge-storage systems.

Upon running the Al/pristine PGS cell to 20 cycles, it is observed that in the first cycle, the specific charge and discharge capacities were 78 and 39 mAh/g, respectively (Figure 6(b)). This resulted in a coulombic efficiency of approximately 50 % and an average voltage of about 1.7 V. However, a significant improvement in the reversibility of the electrochemical process in the second cycle was observed resulting in a coulombic efficiency of 94 %. The observed low coulombic efficiency obtained in the first cycle could be linked to the partial irreversibility of anion intercalation process, suggesting the incomplete deinsertion of the intercalated species from the pristine PGS. By heating pristine PGS at 900°C for 2 h, the coulombic efficiency in the first cycle improved to 70 % and averaged at 97 % from the 2nd to 20th cycle (Figure 6(b)). These enhancements in both coulombic efficiency and specific capacity despite at a higher charge/discharge rate strongly suggest higher chloroaluminate ions intercalation/deintercalation reversibility as well as chloroaluminate ion-hosting capability in heat-treated PGS. Although the coulombic efficiency remained above 90 % after 20 cycles, a significant decrease in specific capacity in both cells is

observed. Reasons such as poor sealing of the electrochemical cell, the presence of water (~700 ppm) or impurities in the electrolyte, which could potentially result in unintended side reactions. These issues could be largely improved by utilizing heat-sealable pouch cells accompanied by further purification of the electrolyte.

For PGS cathodes, the ion transportation process can be separated into two parts: (1) AlCl_4^- transport/diffusion in the electrolyte and (2) AlCl_4^- insertion/intercalation in the graphitic materials. Due to the limited open structure available in pristine PGS, the ionic transport/diffusion of AlCl_4^- at the edge of the PGS is expected to be dominant (Figure 7(a)). As observed in Figures 5(c)-(e), heat-treatment of PGS resulted in the formation of pits that disrupted the continuous structure of pristine PGS. Such open structure greatly promoted the effective surface area in contact with the electrolyte, at the same time allowing diffusion of AlCl_4^- into the deeper region of the active materials that in turn allowed more intercalation to occur (Figure 7(b)).

(d) NG-based electrodes

Figures 8(a)-(g) present the SEM images of pristine and sonicated natural graphite from Examples 3(c) and (d) across different sonication time. A typical plate-like morphology with a few hundred microns in size is observed in pristine natural graphite (Figure 8(a)). However, as sonication time increased, fragmentation of large flakes into smaller particles is observed (Figures 8(b)-(f)). Folded edges with a high degree of disorderliness are observed in all sonicated natural graphite. Particles size distributions in Figure 8(h) reveal that the distribution of particles shifted towards smaller diameter region with increasing sonication time. The mean and median particle size of pristine natural graphite was determined as 486 and 473 μm , respectively. At a sonication of 30 minutes, the mean and median particle reduced to 140 and 60 μm , and further down to 92 and 48 μm in 60-minutes sonicated specimen.

The characteristic features in the Raman spectra of carbonaceous materials are the G and D peak/bands, which lie at around 1560 and 1360 cm^{-1} , respectively. The G peak is associated with the bond stretching of the C-C bond (sp^2 hybridization) in both carbon rings and chains of graphitic materials while the D peak is associated with defect-induced double-resonance Raman scattering processes involving the electronic $\pi-\pi^*$ transitions. As observed in Figure 8(i), the Raman spectrum of pristine natural graphite exhibits negligible D peak/band intensity, indicating low defect density in the material. On the other hand, the slight increase in D-peak intensity in sonicated natural graphite could be attributed to the structural disorderliness as observed on the

edge of sonicated natural graphite (Figures 8(b)-(g)). It has been demonstrated that the intensity of the D band relative to that of the G band ($I(D)/I(G)$) is applicable to evaluate the average crystal planar domain size. Based on the $I(D)/I(G)$ obtained (Figure 8 (j)), the average crystal planar domain size of natural and sonicated graphite can be evaluated around 479 and 205 Å, respectively.

Figures 9(a) and (b) illustrate the specific discharge capacity of electrochemical cells using pristine, 30-minutes sonicated, 60-minutes sonicated natural graphite (loading $\sim 1.5 \text{ mg/cm}^2$) and the corresponding coulombic efficiency at different current densities, respectively. In general, the cells demonstrated decreased specific capacity and higher CE with increasing charge-discharge rate. For the Al/pristine NG cell with relatively larger size (~ 10 mesh), it delivered a specific capacity of $\sim 50 \text{ mAh/g}$ (CE $\sim 85 \%$) at a low charge-discharge rate (100 mA/g) and a specific capacity of $\sim 10 \text{ mAh/g}$ (CE $\sim 97 \%$) at a high rate (800 mA/g). For the cells using 30-minutes and 60-minutes sonicated natural graphite, significant improvements in specific discharge capacity across all rates were observed. At 100 mA/g , a specific capacity of ~ 65 (CE $\sim 86 \%$) and $\sim 66 \text{ mAh/g}$ (CE $\sim 82 \%$) was delivered by the cell using 30-minutes and 60-minutes sonicated graphite, respectively. Even at a high rate of 800 mA/g , the cell could still deliver a capacity of ~ 32 (CE $\sim 97 \%$) and $\sim 38 \text{ mAh/g}$ (CE $\sim 96 \%$) for 30-minutes and 60-minutes sonicated NG, respectively. These results indicate a strong correlation between specific capacity/rate capability of a cell and the size of NG flakes. In addition, the open structure at the edge of the sonicated graphite particles (observed in Figures 8(b)-(g)) could have facilitated the diffusion and intercalation of AlCl_4^- , resulting in improved performance of the cells using sonicated graphite.

To investigate the effects of loading on the electrochemical performance of the cell, 30-minutes sonicated NG was selected as the active material due to better capacity recovery and higher coulombic efficiency compared with 60-minutes sonicated NG (Figures 9(a) and (b)). Figures 9 (c) and (d) present the specific discharge capacity of the Al/30-min sonicated NG cell with loadings ranging from ~ 1.0 to $\sim 2.5 \text{ mg/cm}^2$, and the corresponding coulombic efficiency at different current densities, respectively. With a decrease in loading of active materials, a significantly higher specific capacity but lower CE was observed across all rates. At a higher loading of 2.6 mg/cm^2 , the cell delivered a specific capacity of $\sim 69 \text{ mAh/g}$ (CE $\sim 93 \%$) at a low charge-discharge rate (100 mA/g) and a specific capacity of $\sim 15 \text{ mAh/g}$ (CE $\sim 98 \%$) at a high rate of 800 mA/g . When the loading was reduced to 0.9 mg/cm^2 , the specific capacity significantly improved to $\sim 83 \text{ mAh/g}$ (CE $\sim 81\%$) at 100 mA/g and to $\sim 51 \text{ mAh/g}$ (CE $\sim 97\%$) at 800 mA/g . This fast-charge capability of Al-ion batteries using AlCl_3 /urea-based electrolyte is unprecedented in the field.

To evaluate the long-term cyclability, galvanostatic charge-discharge tests (started at 100 mA/g for 20 cycles, and at 600 mA/g for up to 1000 cycles) were performed using a newly assembled Al/30-minutes sonicated NG cell with a cathode loading of 1.0 mg/cm² and the results are presented in Figure 10. Initial cycling at 100 mA/g was necessary for stabilization of the cell. As observed in Figure 10(a), low CE (~90 %) observed in the initial cycles suggests side reactions during this period. As the specific charge-discharge rate increased to 600 mA/g, the specific capacity remained stable at ~50 mAh/g and maintained a coulombic efficiency of ~95% across the 1000 cycle. In addition, the charge and discharge curves of the cell recorded at the 500th and 1000th cycle showed negligible differences with two distinct discharge voltage plateaus in the ranges 2.0–1.8 V and 1.6–1.3 V, respectively (Figure 10(b)).

(e) MWEg electrode

Based on the results obtained above, graphitic materials with open structure seemed to enhance the specific capacity as well as the rate capability of Al-ion cells. Among potential graphitic materials, attention was given to expandable graphite (EG) because of its extensive open structure and low bulk density. In general, EG is produced by rapid heating of graphite intercalation compounds (GICs) through techniques such as furnace heating, coupled plasma, laser irradiation and microwave irradiation. The rapid increase in temperature results in the abrupt ejection or decomposition of intercalated species in between the superposed graphene sheets, causing a marked expansion in the c-direction and formation of an intumescent structure. In this study, the exfoliation of graphite through microwave irradiation was chosen because of the ease of conducting the experiment at room temperature, short irradiation time, and less energy consumption. In addition, it has been reported that the exfoliation of GICs via microwave irradiation showed no significant difference in resultant EG compared with those prepared by rapid heating. Figure 11(a) presents the MWEg obtained in Example 3(e). In further reducing the particle size of microwave-exfoliated graphite (MWEg), the resultant MWEg was further sonicated for 2 hours and a free-standing sonicated MWEg was fabricated through vacuum filtration (Figure 11(b)). The results obtained from the rate capability tests of an Al-ion battery using the free-standing sonicated MWEg as the cathode is illustrated in Figure 11(c). The cell could deliver a specific capacity of ~45 mAh/g at 50 mA/g. Despite suffering from drops in specific capacity with increasing charge/discharge rate, the cell retained a significant portion of its capacity when the rate was lowered. This cell also demonstrated a relatively high coulombic efficiency compared with other NG-based Al-ion cells.

(f) Effect of 1,2-dichloroethane (DCE) addition

Despite the high reversibility of batteries using AlCl_3 /urea DESs, the ionic conductivity of the electrolyte remains lower than that of AlCl_3 /[EMIm]Cl at room temperature. The use of additives, such as toluene and acetamide was considered. However, the effect was found to be limited. A potential additive (1,2-dichloroethane, DCE) was reported as lowering the viscosity and improving the conductivity of AlCl_3 -urea DESs while maintaining high concentrations of ionic species in the anolyte. The CV of the electrolyte with various concentration of DCE as additive was conducted and the results are presented in Figure 12(a). From these results, the mixture with 10 vol.% DCE addition exhibited significant oxidation across all oxidation potential range; suggesting a reduction in the electrochemical stability window due to 10 vol.% DCE addition. At a lower amount of DCE additions (5 and 2.5 vol %), a slight increase in the oxidation of the mixture was still observed (Figure 12(a), inset) compared to no addition. However, the amount of oxidation in the mixtures with lower DCE addition is comparatively insignificant when the oxidation of active materials is considered (see Figure 4(b)).

To investigate the electrochemical performance of a cell using the electrolyte with DCE addition, a cell was fabricated using 30-minutes sonicated NG as the cathode (1.4 mg/cm^2) and a mixture of AlCl_3 -urea (AlCl_3 /urea = 1.3 by mole)-DCE (5% by volume) as the electrolyte. A relatively moderate initial cycling condition was applied to stabilize the cell. The result of the galvanostatic charge/discharge test is presented in Figure 12(b). The specific capacities delivered by the cell using AlCl_3 -urea-DCE electrolyte was at $\sim 30 \text{ mAh/g}$ at 600 mA/g with an average CE of $\sim 98\%$ after the initial cycling round. These results indicate an improved CE of the cell with an adequate amount of DCE additions.

(g) Sulfide and oxide-based electrodes

In addition to graphitic/carbonaceous cathode materials as presented in previous examples, other material such as metal oxides, metal sulfides, and non-metal sulfides may also be used as cathode materials in Al batteries. To investigate the electrochemical performance of sulfide/oxide cathode in AlCl_3 -urea DES, three different Al battery systems that cover a metal sulfide (MoS_2 , Example 3(f)), a metal oxide (V_2O_5 , Example 3(g)), and a non-metal sulfide (SeS_2 , Example 3(h)) were prepared and tested. The results of each system are presented in Figure 13.

Figure 13(a) illustrates the discharge voltage profile of an Al/AlCl_3 -urea/ MoS_2 system across various cycles. In the initial cycle, the cell exhibited a specific discharge capacity of $\sim 83 \text{ mAh/g}$

(at 25 mA/g) with an average voltage of ~ 0.51 V. The specific discharge capacity stabilized at around ~ 30 mAh/g between the 20th and 30th cycle, followed by an increase to 104 mAh/g in the 47th cycle. Such an increase in specific capacity upon cycling maybe the result of the increasing proportion of previously unutilized active materials that was not actively involved in the electrochemical reactions. Insertion of Al^{3+} into the MoS_2 microstructure is considered as charge-storage mechanism during charging of an Al/ MoS_2 battery system.

For a V_2O_5 cathode, the initial specific discharge capacity obtained recorded a value of ~ 108 mAh/g with an average discharge voltage of 0.69 V at 25 mA/g (Figure 13(b)). It was suggested that only the top 10 nm-thickness of V_2O_5 particles participate actively in the electrochemical reactions of chloroaluminate-based Al batteries. Under such condition, the obtainable theoretical specific capacity of the V_2O_5 electrode is reported as 106.2 mAh/g. This value is in a good agreement with the initial specific capacity obtained. The reversible specific capacity of Al/ V_2O_5 batteries remained at ~ 40 mAh/g with subsequent cycling up to 50 cycles. Similar to the charge-storage mechanism of Al/ MoS_2 system, insertion/de-insertion of Al^{3+} into/from V_2O_5 is generally considered as the dominating mechanism during the charge/discharge process.

The discharge voltage profile for an Al/ SeS_2 system utilizing the present AlCl_3 -urea DES is presented in Figure 13(c). This system exhibited an excellent specific discharge capacity of ~ 112 mAh/g with an average discharge voltage of 1.53 V at 50 mA/g in the first cycle. This average discharge voltage is reportedly the highest among existing literature on metal/non-metal oxides/sulfide cathodes utilized in non-aqueous Al batteries. Despite the fact that the specific capacity decreased (to ~ 35 mAh/g) with subsequent cycling, the discharge voltages remained reasonably high across the cycles. Given the fact that there is no current literature on Al/ SeS_2 battery utilizing chloroaluminate electrolyte system, further investigations will be conducted to elucidate the charge/discharge mechanism of this system.

In summary, it was demonstrated herein that an Al-ion battery could be prepared using affordable AlCl_3 /amide-based (e.g. urea) deep eutectic solvents as the electrolyte, aluminum metal as the anode, and graphitic materials (e.g. pristine pyrolytic/natural graphite, treated pyrolytic/natural graphite (through heat-treatment for pyrolytic graphite; ultrasonication and microwave exfoliation for natural graphite)), and sulfide/oxide material (e.g. MoS_2 , V_2O_5 , and SeS_2) as the cathode. In general, two stable discharge plateaus at 2.0-1.8 V and 1.6-1.3 V are observed in assembled Al/graphitic material batteries. For sulfide/oxide material electrodes, the cell performance varied across different systems: Al/ SeS_2 battery exhibited the highest discharge voltage, Al/ MoS_2 and

Al/V₂O₅ exhibited reasonable capacity/cyclability. At the anode, it is considered that both Al₂Cl₇⁻ and AlCl₂·(urea)_n⁺ species are responsible for electrodeposition/stripping of Al in AlCl₃/urea DES. At the cathode, intercalation/deintercalation of AlCl₄⁻ into/from the graphitic cathode is the dominating mechanism. On the other hand, the insertion/de-insertion of Al³⁺ into/from sulfide/oxide-based electrode is considered the main operating mechanism of Al/sulfide and Al/oxide batteries. For the pyrolytic graphite-based cathode, heat treatment was found to be extremely effective in improving the electrochemical cell's specific capacity and rate capability. For the natural graphite-based cathode, the performance of the batteries was significantly affected by the size of natural graphite flakes used; with a smaller size resulting in a higher specific capacity and rate capability. In addition, ultrasonication of natural graphite flakes is proven an efficient technique that could improve specific capacity as well as the rate capability of the batteries. On the electrolyte side, the addition of a co-solvent (1,2-dichloroethane and toluene) significantly improved the ionic conductivity of the electrolyte (for nearly three times with 20 wt.% addition), which could potentially lead to enhanced specific capacity at a higher charge/discharge rate.

The present document therefore presents an Al-ion electrochemical cells using AlCl₃-urea deep eutectic solvents that can operate at room temperature with aluminum metal as the anode, AlCl₃-urea deep eutectic solvents as the electrolyte and a compatible cathode material (e.g. pristine or treated graphitic materials, oxides and sulfides).

For instance, pyrolytic graphite sheets (both pristine and heat-treated) were used as the cathode, where a heat treatment of the pyrolytic graphite sheets was found to be extremely effective in improving the specific capacity and rate capability, from 40 mAh/g (at 10 mA/g) in pristine pyrolytic graphite sheet, to 55 mAh/g (at 25 mA/g) in heat-treated pyrolytic graphite sheet. Alternatively, ultrasonication of natural graphite (NG) flakes significantly improved the specific charge/discharge capacities from ~50 mAh/g in pristine NG to ~65 mAh/g in sonicated NG at a current density of 100 mA/g (loading: ~1.5 mg/cm²). Even at a high rate of 800 mA/g, the cell could still deliver a capacity of ~32 (30-min sonicated) and ~38 mAh/g (60-min sonicated). When the loading was reduced to 0.9 mg/cm², the highest specific capacity achieved was ~83 mAh/g (CE ~81%) at 100 mA/g and ~51 mAh/g (CE ~97%) at 800 mA/g. This fast-charge capability of Al-ion batteries using AlCl₃/urea-based electrolyte is unprecedented in the field. Furthermore, a cell using free-standing sonicated microwave-exfoliated graphite as cathode material delivered a specific capacity of ~45 mAh/g at 50 mA/g. The high coulombic efficiency obtained in this cell suggested high reversibility of AlCl₄⁻ intercalation/deintercalation.

The present document is also the first to report an electrochemical cell using AlCl_3 -urea electrolyte with addition of a co-solvent (1,2-dichloroethane and toluene). The addition of 1,2-dichloroethane and toluene reduced the viscosity of the electrolyte; resulting in a significant improvement in ionic conductivity (about three-fold increase with 20 wt.% co-solvent additions at room temperature). Improvement in coulombic efficiency of the cell is observed with the addition of as low as 5 vol.% of 1,2-dichloroethane.

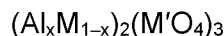
Demonstration is also presented herein of the fast-charge capability of an Al/graphite cell using an AlCl_3 /urea-based electrolyte that delivered a stable specific capacity at ~ 50 mAh/g at 600 mA/g across 1000 cycles. Indeed, in this region, negligible changes in the battery's capacity were observed. Moreover, the cell achieved appreciable specific capacities (~ 70 and ~ 50 mAh/g) even at very high rates (400 and 800 mA/g, corresponding to fully charge/discharge time of 10.5 and 3.8 min, respectively) indicating the fast-charge capability of the cells. This represents a significant breakthrough in this type of battery as none of the batteries using similar chemistry in the literature thus far reported could sustain such high rates.

Finally, the electrochemical performance of Al/sulfide (MoS_2 and SeS_2) and Al/oxide (V_2O_5) batteries were demonstrated using an AlCl_3 /urea-based electrolyte. The highest specific capacity obtained for Al/ AlCl_3 -urea/ MoS_2 system was 104 mAh/g (47th cycle), for Al/ AlCl_3 -urea/ SeS_2 system was 112 mAh/g (1st cycle), and for Al/ AlCl_3 -urea/ V_2O_5 system was 108 mAh/g (1st cycle). The average discharge voltage obtained in the Al/ AlCl_3 -urea/ SeS_2 system is reportedly the highest (~ 1.5 V) among existing literature on non-aqueous Al batteries employing oxide/sulfide electrodes.

Numerous modifications could be made to any of the embodiments described above without departing from the scope of the present invention. Any references, patents or scientific literature documents referred to in this document are incorporated herein by reference in their entirety for all purposes.

CLAIMS

1. An electrochemical cell comprising an electrolyte, an anode and a cathode, wherein the electrolyte comprises AlCl_3 and an amide-based compound, and wherein the anode comprises metallic aluminum.
2. The electrochemical cell of claim 1, wherein the AlCl_3 and amide-based compound form a deep eutectic solvent.
3. The electrochemical cell of claim 1 or 2, wherein the amide-based compound is of formula $\text{R}^1\text{C}(\text{O})\text{R}^2$, wherein R^1 is NH_2 or $\text{C}_{1-6}\text{alkylNH}$ and R^2 is NH_2 , $\text{NHC}_{1-6}\text{alkyl}$ or $\text{C}_{1-6}\text{alkyl}$.
4. The electrochemical cell of claim 3, wherein R^1 and R^2 are each NH_2 or $\text{NHC}_{1-3}\text{alkyl}$.
5. The electrochemical cell of claim 3, wherein R^1 and R^2 are each $\text{NHC}_{1-3}\text{alkyl}$.
6. The electrochemical cell of claim 3, wherein R^1 is NH_2 or $\text{C}_{1-3}\text{alkylNH}$ and R^2 is $\text{C}_{1-3}\text{alkyl}$.
7. The electrochemical cell of claim 1 or 2, wherein the amide-based compound is urea (R^1 and R^2 are each NH_2).
8. The electrochemical cell of claim 1 or 2, wherein the amide-based compound is *N,N'*-dimethylurea.
9. The electrochemical cell of claim 1 or 2, wherein the amide-based compound is acetamide.
10. The electrochemical cell of any one of claims 1 to 9, wherein the electrolyte further comprises a co-solvent.
11. The electrochemical cell of claim 10, wherein the co-solvent is 1,2-dichloroethane.
12. The electrochemical cell of any one of claims 1 to 11, wherein the cathode comprises an electrochemically active material selected from:
 - graphite;
 - CuS , Ni_3S_2 , Mo_6S_8 , MoS_2 , SeS_2 , polypyrrene, zeolite-templated carbon and vanadium oxide; and
 - a spinel oxide of the formula:



wherein:

M represents $M_2^aM_3^bM_4^c$, wherein:

M_2 is a bivalent metal element selected from the group consisting of Mg, Ca, Sr and Ba;

M_3 is a trivalent metal element selected from the group consisting of Sc, Y, Ga and In; and

M_4 is a tetravalent metal element selected from the group consisting of Zr and Hf;

M' is a hexavalent metal element; and

a, b, c and x are such that $0 \leq a < 1$, $0 \leq b < 1$, $c = a$, and $0 \leq x < 1$, wherein:

$$(2a/(1-x) + 3b/(1-x) + 4c/(1-x)) = 3.$$

13. The electrochemical cell of claim 12, wherein the cathode electrochemically active material comprises graphite.
14. The electrochemical cell of claim 13, wherein said graphite comprises pyrolytic, natural or exfoliated graphite.
15. The electrochemical cell of claim 14, wherein said pyrolytic graphite is pristine.
16. The electrochemical cell of claim 14, wherein said pyrolytic graphite is heat-treated.
17. The electrochemical cell of claim 14, wherein said natural graphite is pristine.
18. The electrochemical cell of claim 14, wherein said natural graphite is ultrasonicated.
19. The electrochemical cell of claim 14, wherein said exfoliated graphite is sonicated microwave-exfoliated graphite.
20. The electrochemical cell of claim 19, wherein when the cathode comprises sonicated microwave-exfoliated graphite as electrochemically active material, then the cathode is a free-standing cathode.
21. The electrochemical cell of claim 12, wherein the cathode electrochemically active material comprises a vanadium oxide selected from VO_2 or V_2O_5 , preferably V_2O_5 .

22. The electrochemical cell of claim 12, wherein the cathode electrochemically active material comprises MoS_2 .
23. The electrochemical cell of claim 12, wherein the cathode electrochemically active material comprises SeS_2 .
24. The electrochemical cell of claim 12, wherein the cathode electrochemically active material comprises the spinel oxide of the formula $(\text{Al}_x\text{M}_{1-x})_2(\text{M}'\text{O}_4)_3$, wherein x, M and M' are as defined in claim 12.
25. The electrochemical cell of claim 24, wherein M' is W or Mo.
26. The electrochemical cell of any one of claims 21 to 25, wherein said cathode further comprises a conductive carbon.
27. The electrochemical cell of any one of claims 12 to 26, wherein cathode further comprises a binder.
28. A battery comprising at least one electrochemical cell as defined in any one of claims 1 to 27.
29. The battery of claim 28, wherein said battery is an aluminum-ion battery.
30. The battery of claim 28 or 29, for use in supplying electric power to a consumer electronic device.
31. The battery of claim 28 or 29 for use in supplying electric power to a hybrid or electric vehicle.
32. The battery of claim 28 or 29 for use in storing electrical energy within an electrical power grid.
33. A method of supplying electric power to an external device comprising:
 - (a) providing an electrochemical cell as defined in any one of claims 1 to 27;
 - (b) connecting the electrochemical cell to the external device; and
 - (c) allowing the electric current to flow from the electrochemical cell to the external device.

34. The method of claim 33, wherein the electrochemical cell is a component of a battery.
35. The method of claim 33 or 34, wherein said an external device is a consumer electronic device.
36. The method of claim 33 or 34, wherein said an external device is a hybrid or electric vehicle.
37. The method of claim 34, wherein the battery is used in storing electrical energy within an electrical power grid, and the device is connected to the electrical power grid.

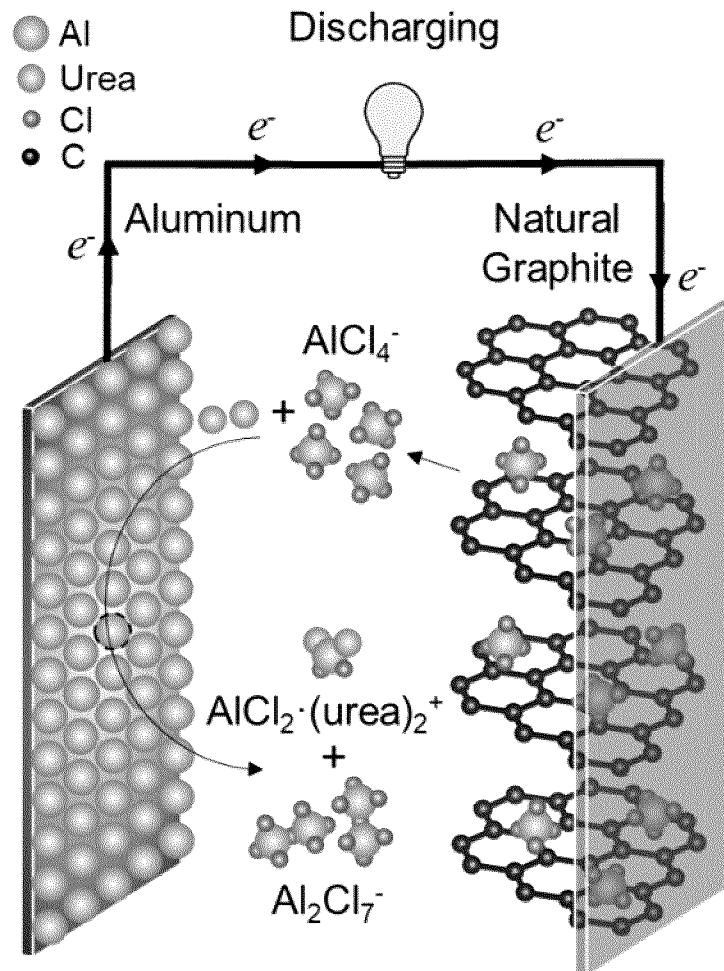
FIGURE 1

FIGURE 2

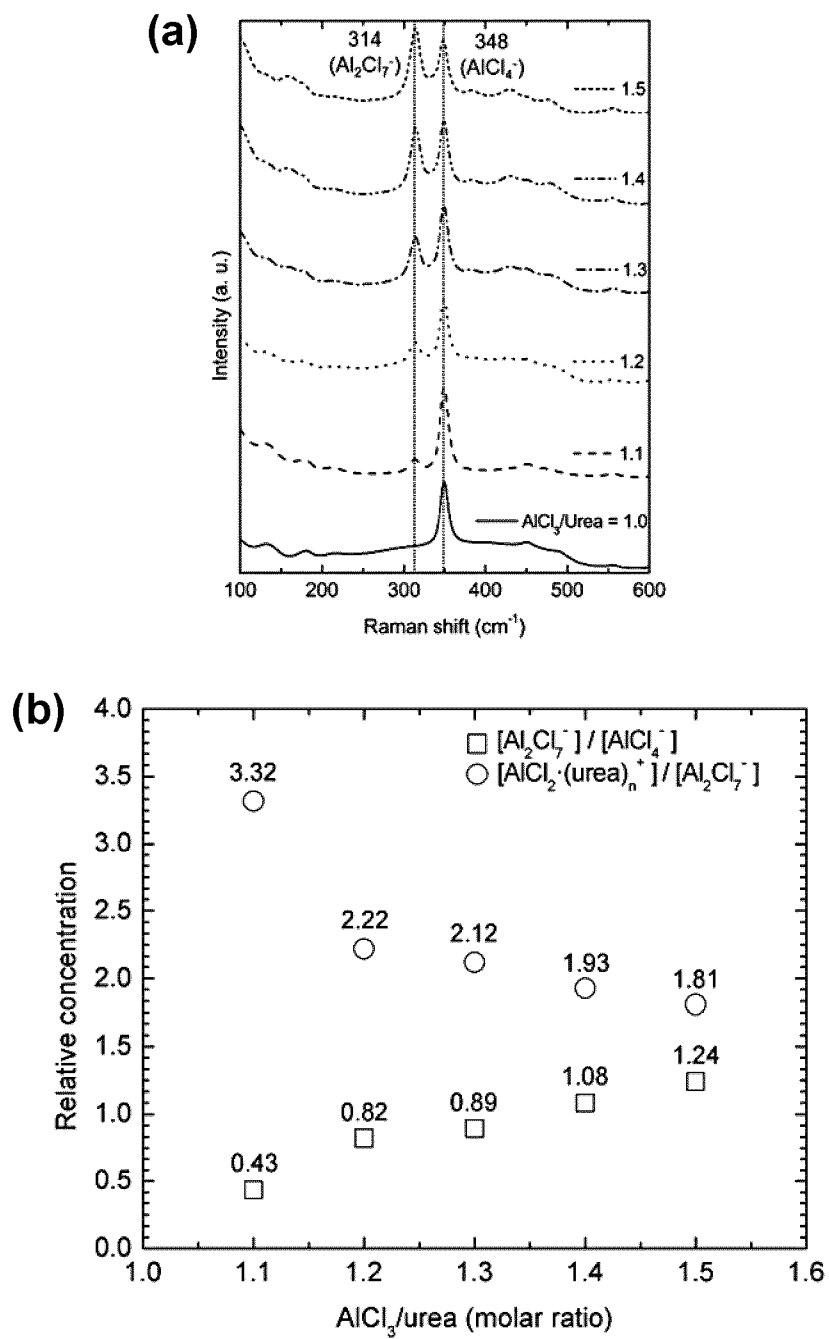


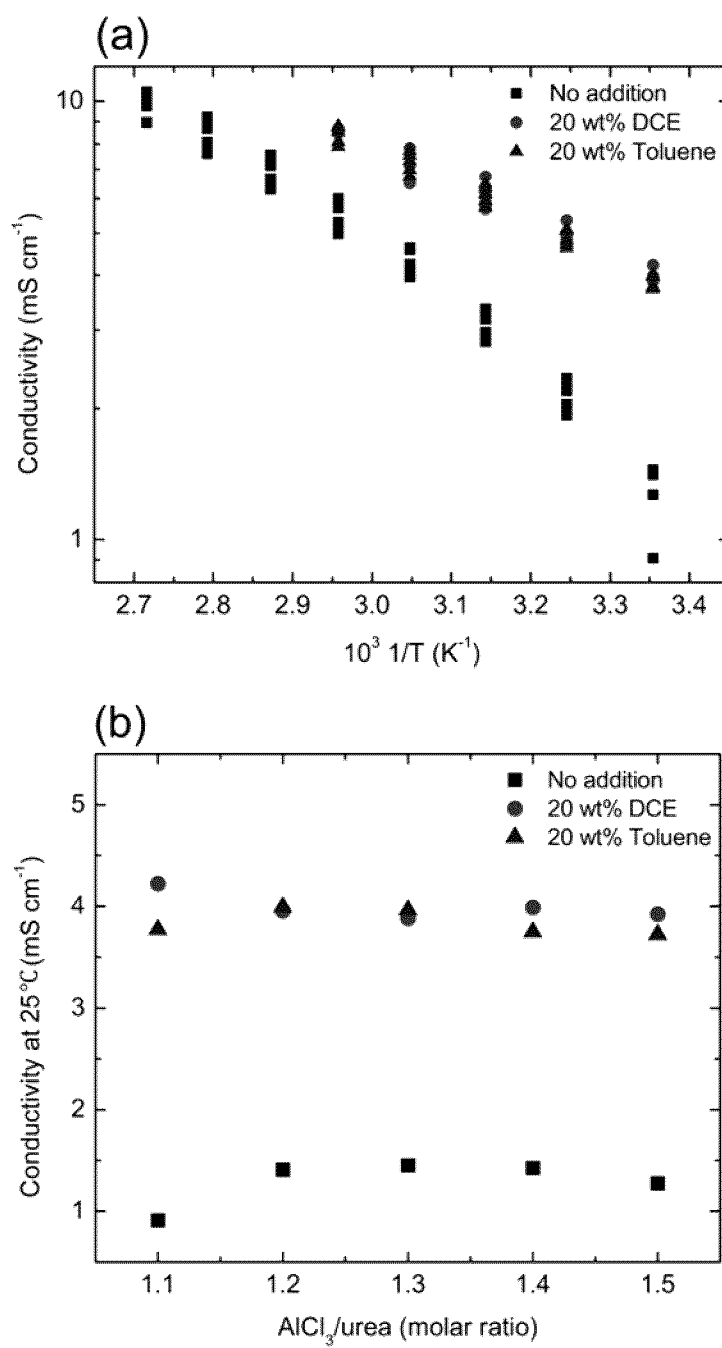
FIGURE 3

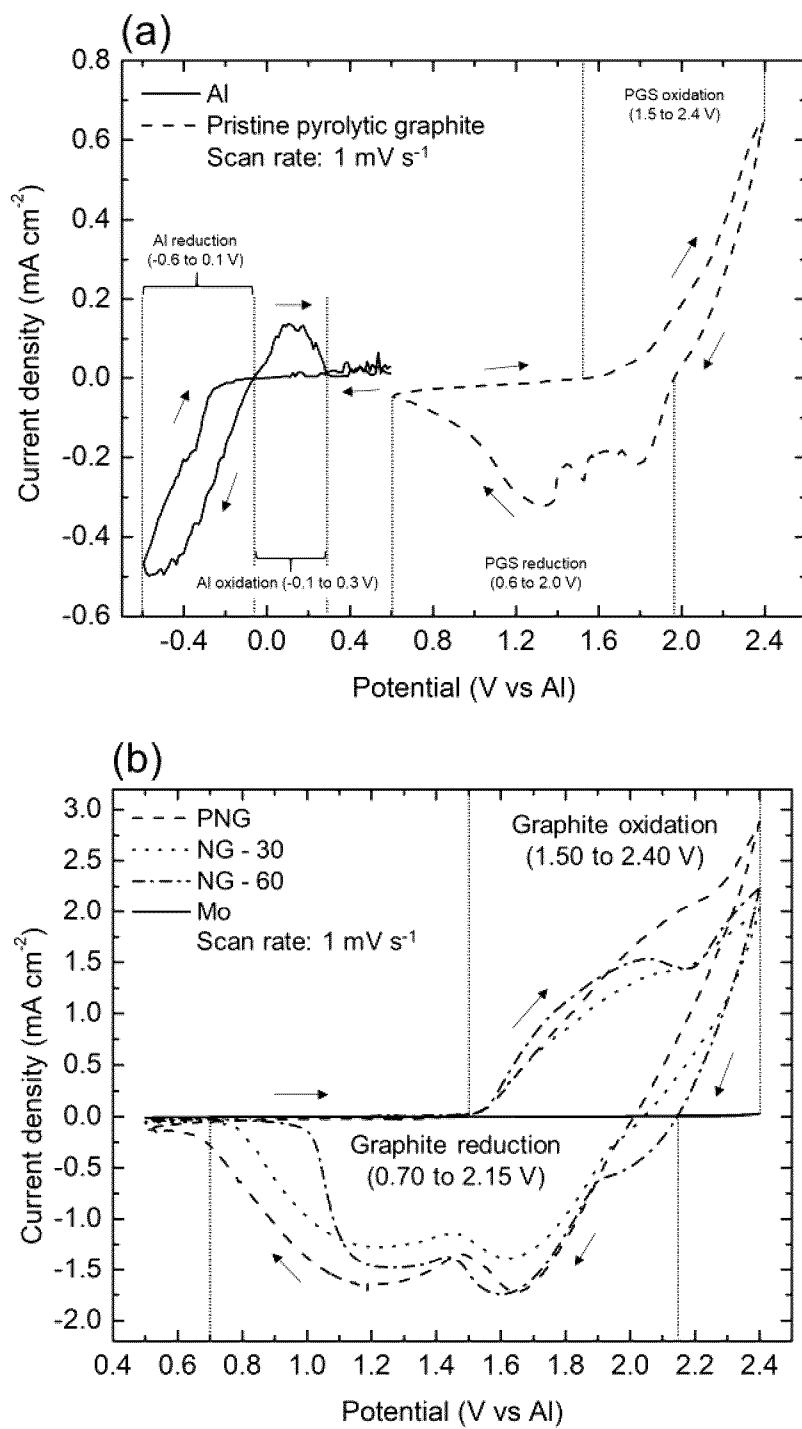
FIGURE 4

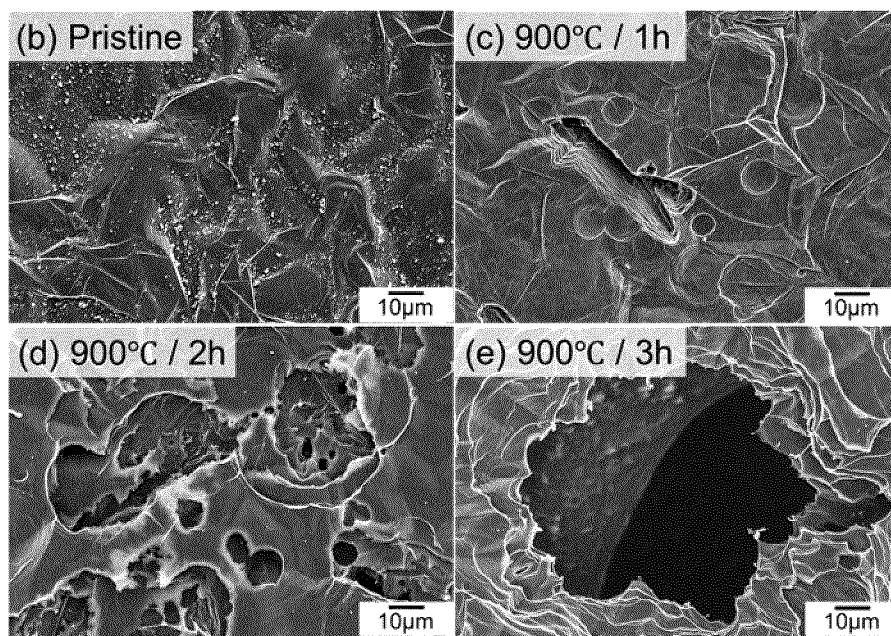
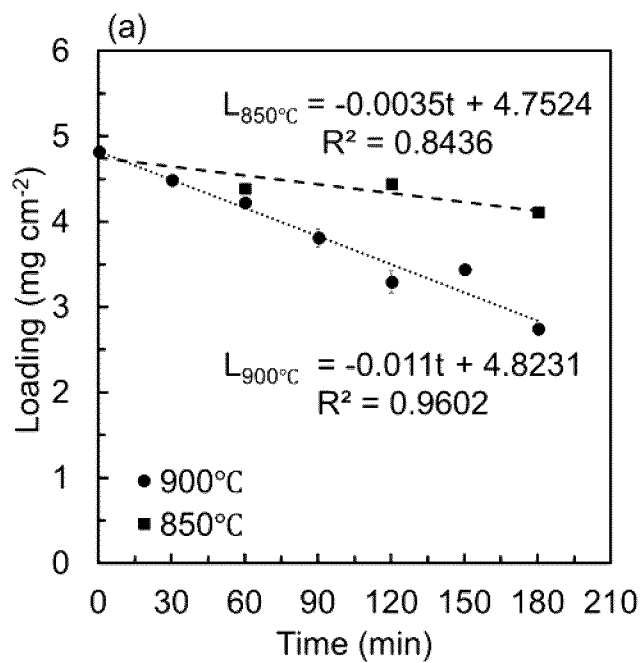
FIGURE 5

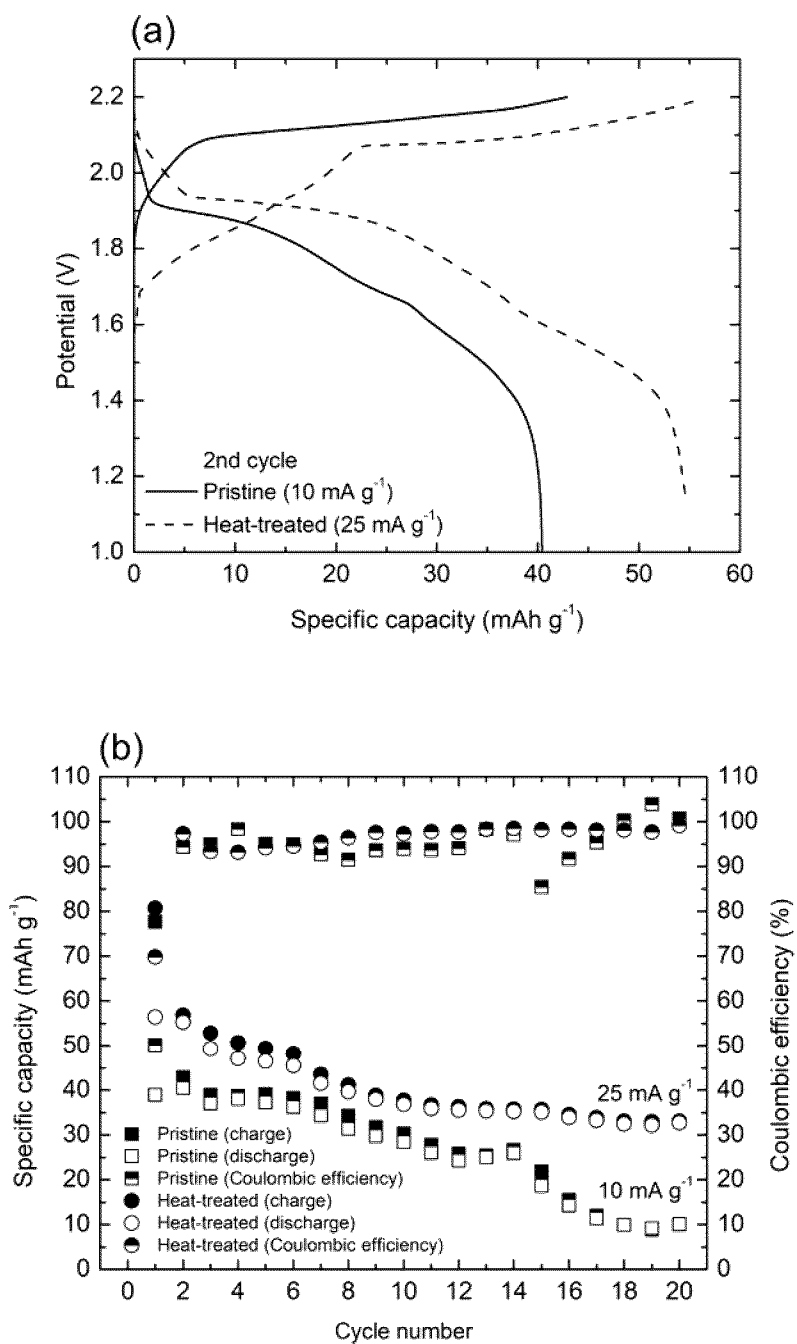
FIGURE 6

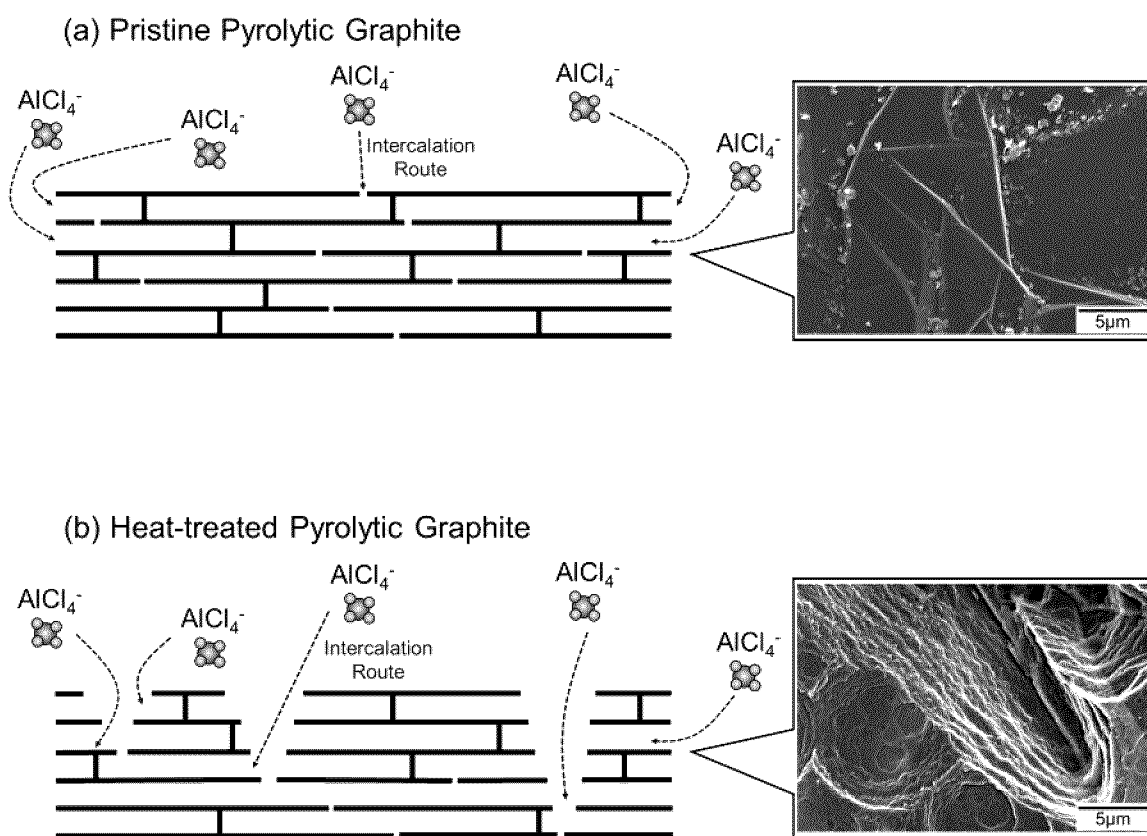
FIGURE 7

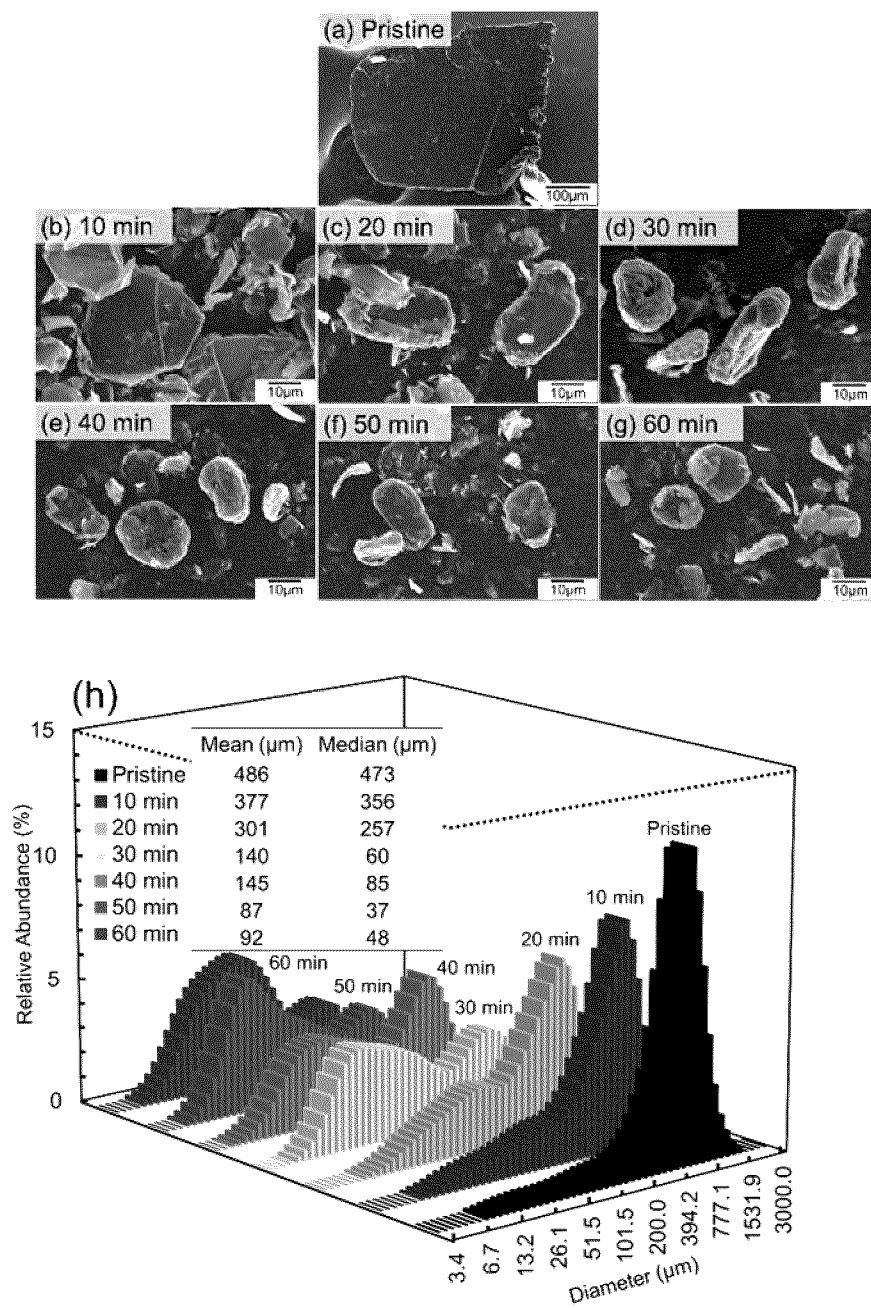
FIGURE 8 (a) to (h)

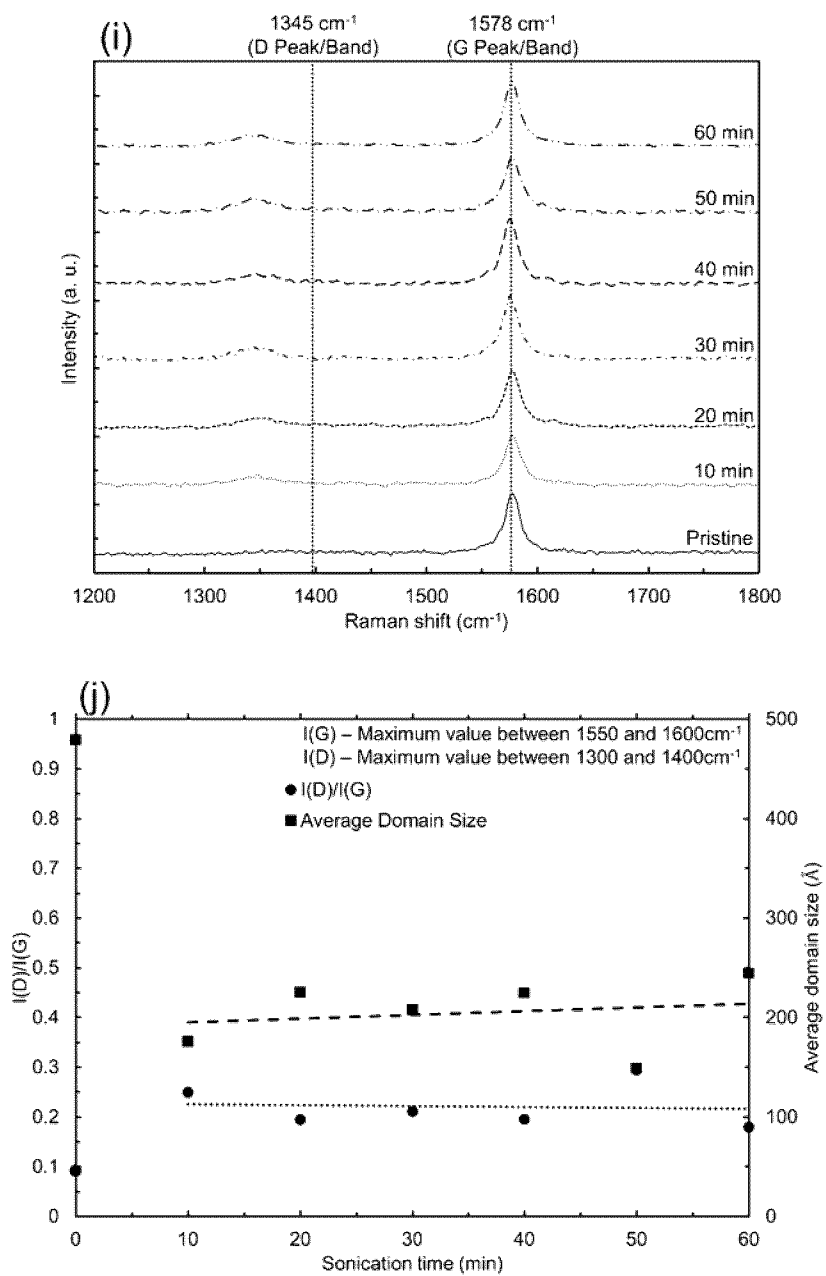
FIGURE 8 (i) and (j)

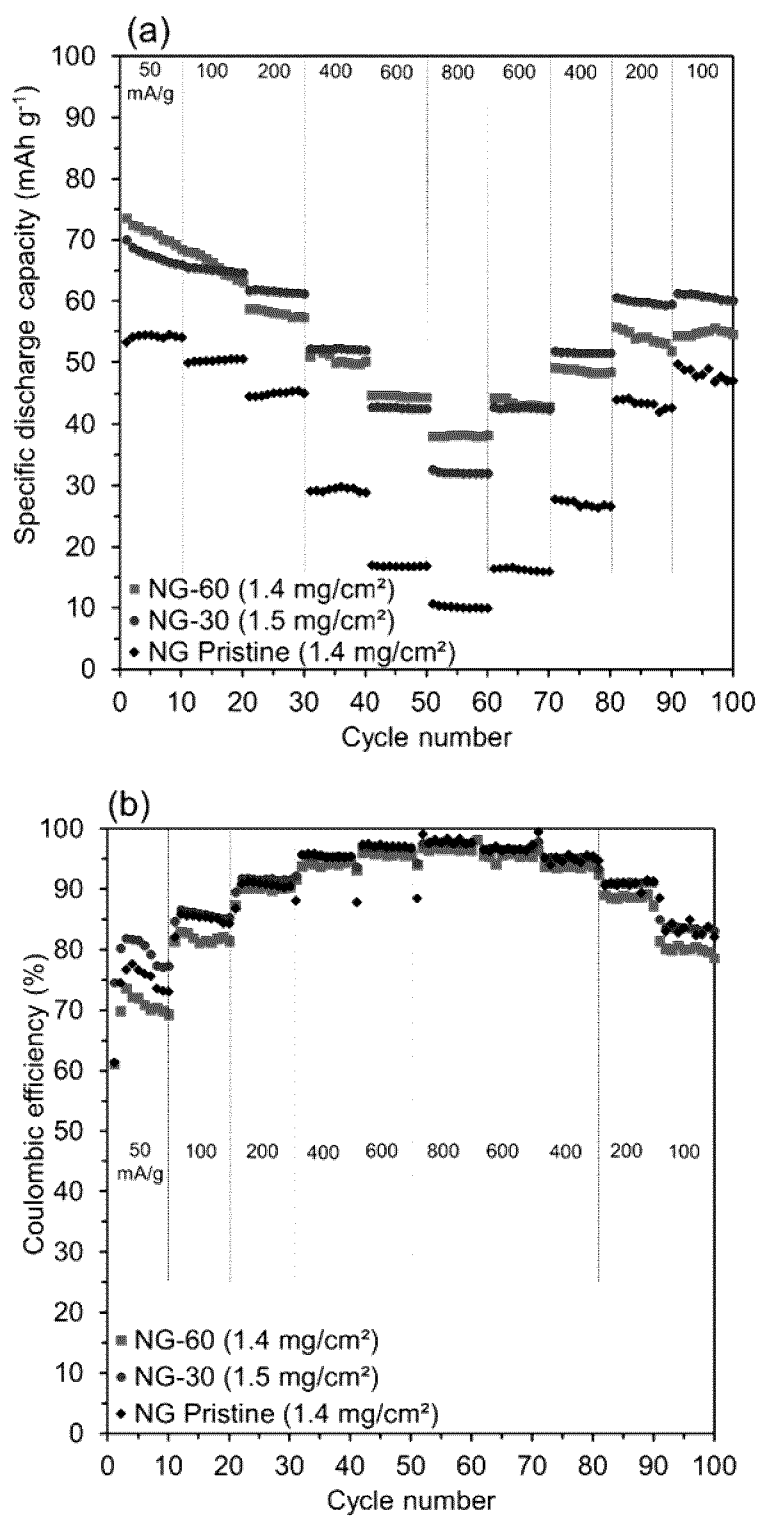
FIGURE 9 (a) and (b)

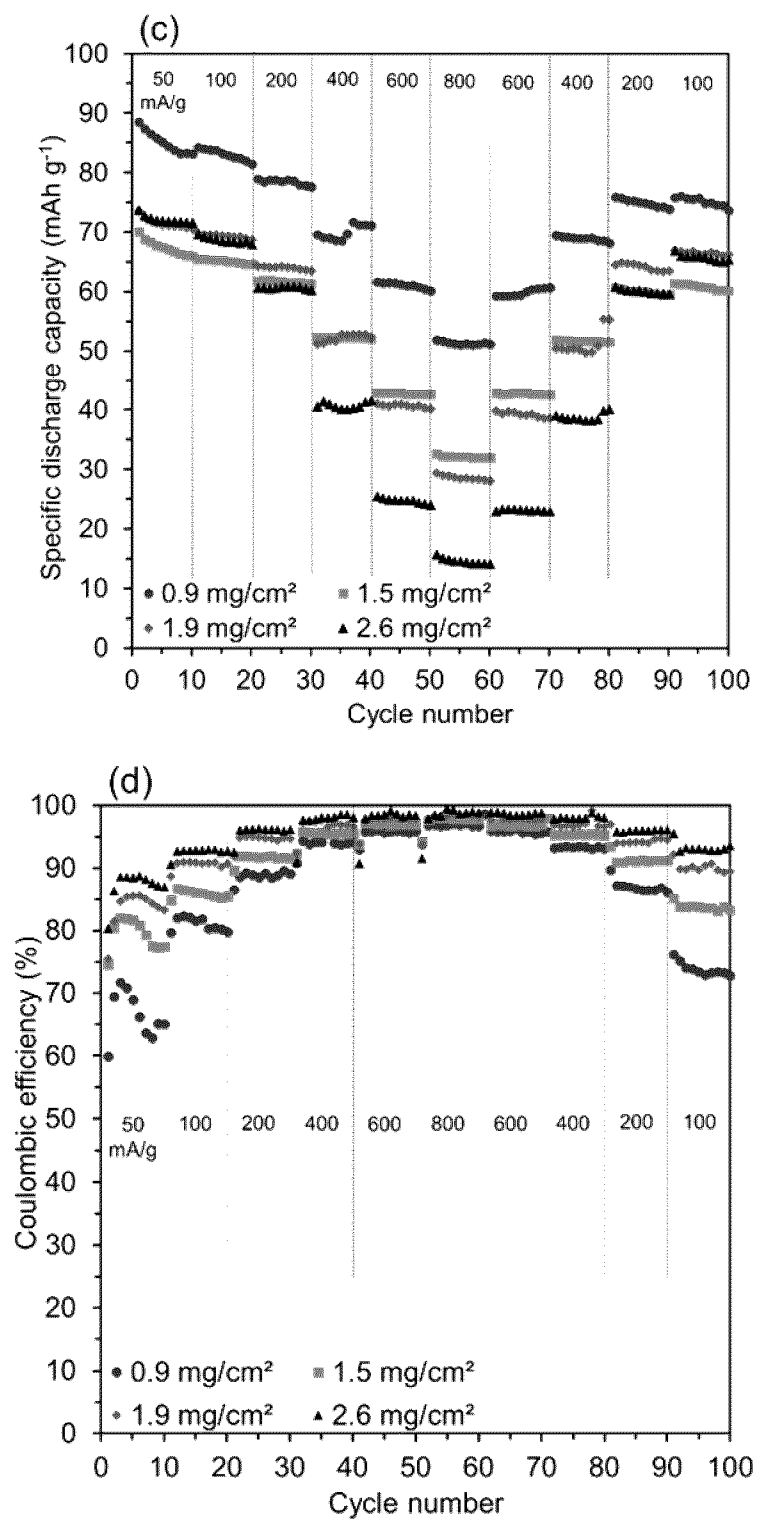
FIGURE 9 (c) and (d)

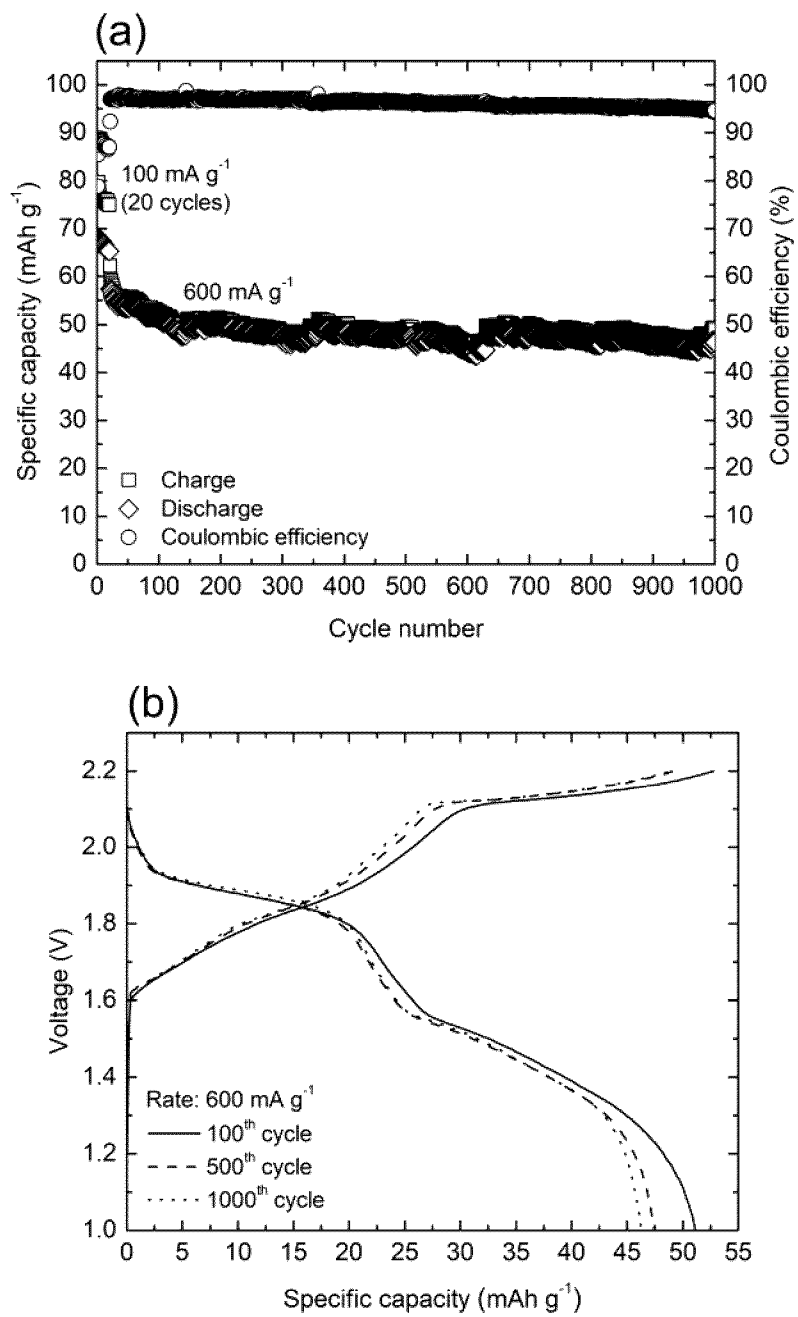
FIGURE 10

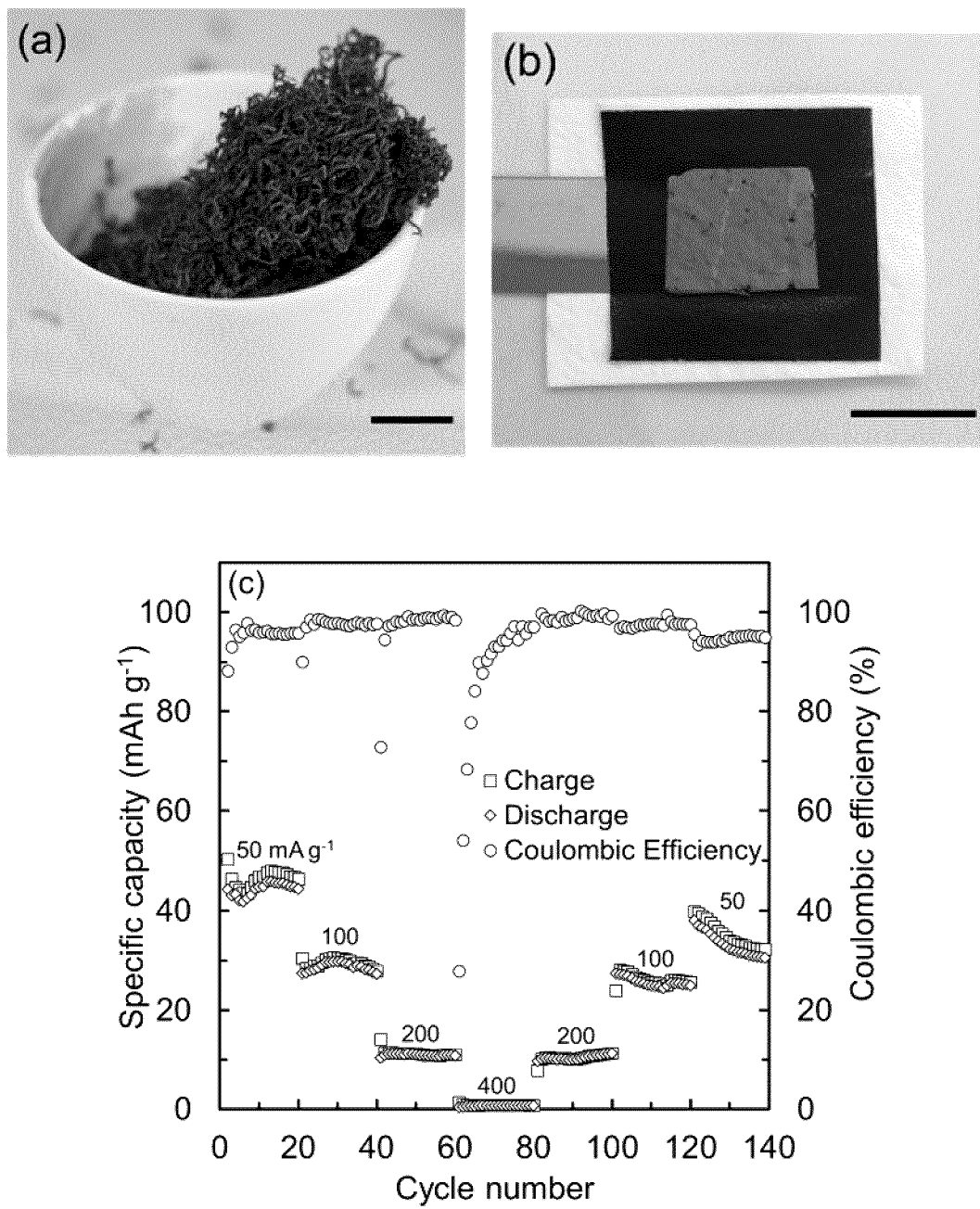
FIGURE 11

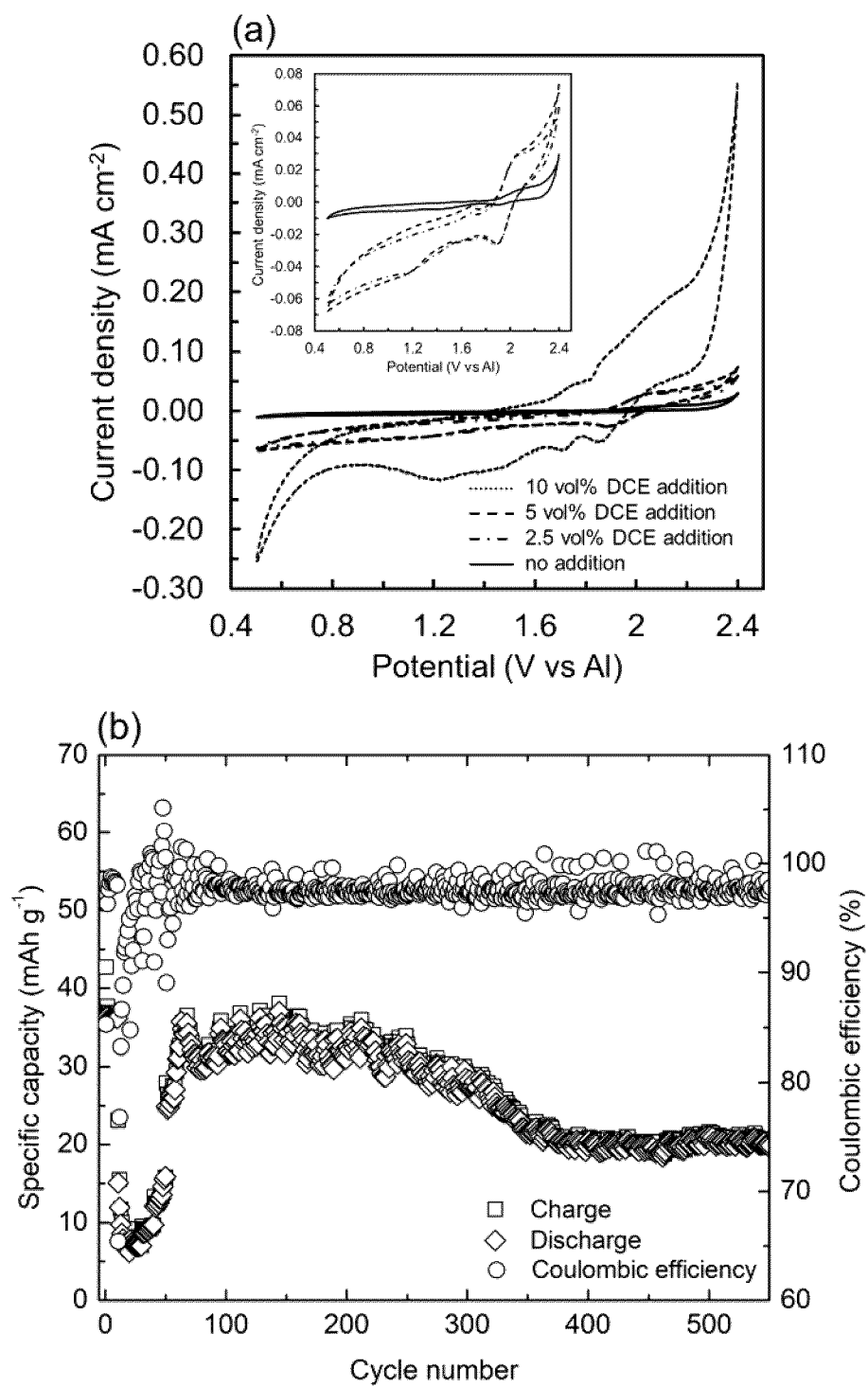
FIGURE 12

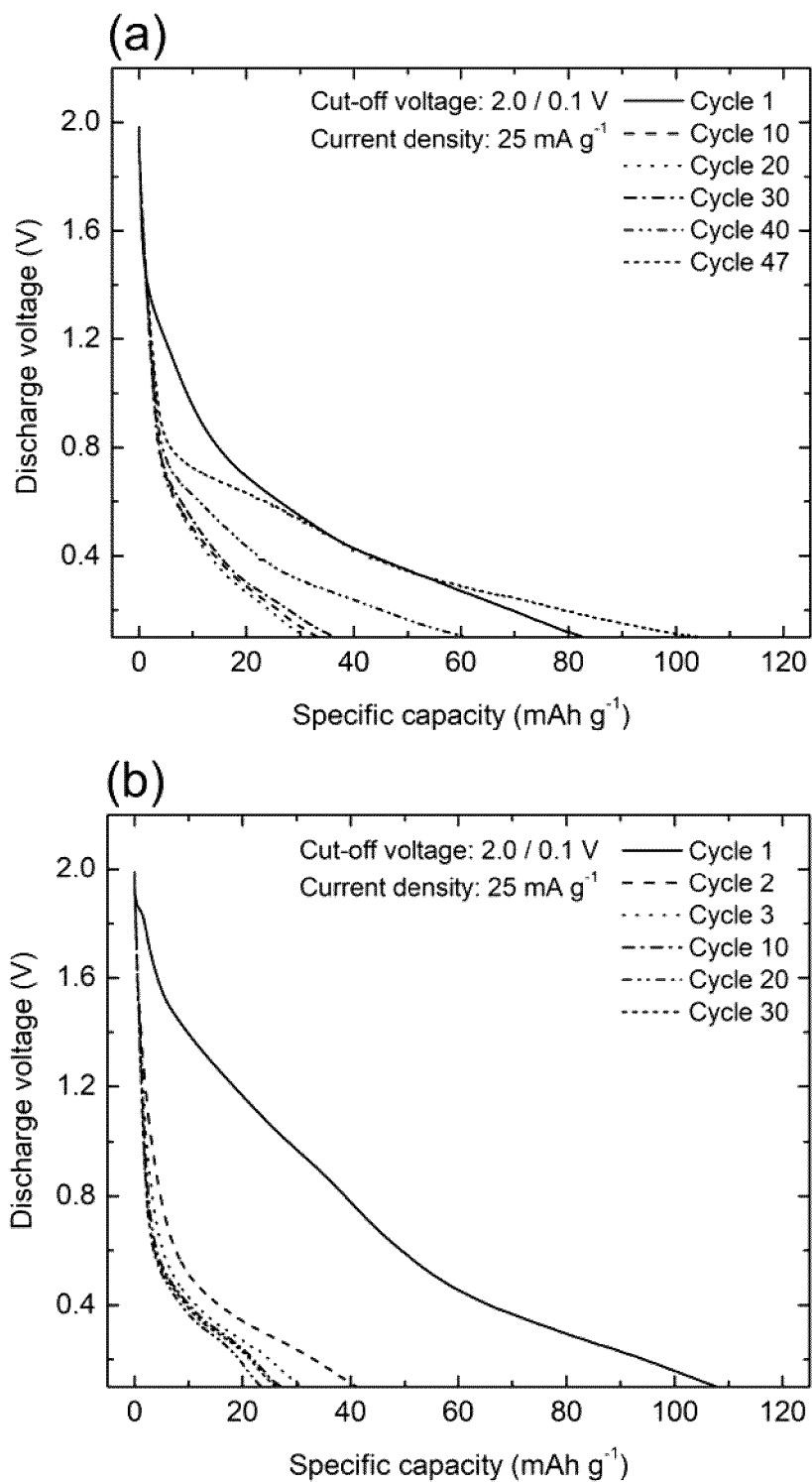
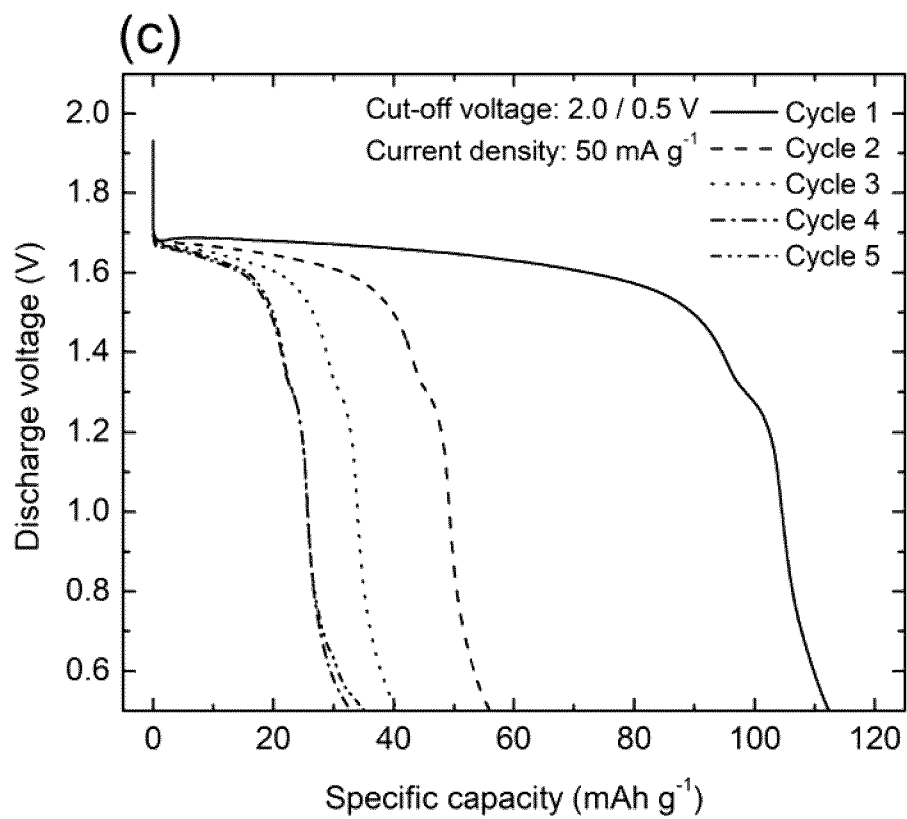
FIGURE 13(a) and (b)

FIGURE 13(c)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CA2019/051334

A. CLASSIFICATION OF SUBJECT MATTER

IPC: **H01M 10/054** (2010.01) , **H01M 10/056** (2010.01) , **H01M 10/44** (2006.01) , **H01M 4/134** (2010.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC (2010.01): H01M 10/054, H01M 10/056, H01M 4/134

IPC (2006.01): H01M 10/44

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

IPC (2006.01): H01M 10/40, H01M 10/36

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)

Databases: QUESTEL, Canadian Patent Database, CIPO Library Discovery Tool

Keywords: battery, cell, electrochemical, aluminum, aluminium, amide, acetamide, urea, carbamide, AlCl₃, aluminum chloride, aluminium chloride

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	WO 2017/106337 A1 (DAI <i>et al.</i>) 22 June 2017 (22-06-2017) *whole document*	1-14, 27-37 15-26
X Y	JIAO <i>et al.</i> , "A rechargeable Al-ion battery: Al/molten AlCl ₃ -urea/graphite", <i>Chem. Commun.</i> , Volume 53 (2017), Pages 2331-2334.	1-14, 27-37 15-26
X Y	ANGELL <i>et al.</i> , "High Coulombic efficiency aluminum-ion battery using an AlCl ₃ -urea ionic liquid analog electrolyte", <i>PNAS</i> , Volume 114, No. 5 (31 January 2017), Pages 834-839.	1-14, 27-37 15-26
Y A	KRAVCHYK <i>et al.</i> , "Efficient Aluminum Chloride-Natural Graphite Battery", <i>Chem. Mater.</i> Volume 29 (2017), Pages 4484-4492.	15-26 1-14, 27-37
Y A	WO 2018/071602 A1 (MUKHERJEE, <i>et al.</i>) 19 April 2018 (19-04-2018) *whole document*	15-26 1-14, 27-37

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Date of the actual completion of the international search

18 November 2019 (18-11-2019)

Date of mailing of the international search report

19 November 2019 (19-11-2019)

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INTERNATIONAL SEARCH REPORT

International application No.

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