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(71) **Applicant:** CORNELL UNIVERSITY [US/US]; Cornell Center for Technology Enterprise & Commercialization, 395 Pine Tree Road, Suite 310, Ithaca, New York 14850 (US).

(72) **Inventors:** ARCHER, Lynden A.; 1032 Hanshaw Road, Ithaca, New York 14850 (US). XU, Shaomao; 319 Highland Road, Apt. 5F1, Ithaca, New York 14850 (US). AL SADAT, Wajdi Issam; 19 Baker Hill Road, Apt. 3, Freeville, New York 13068 (US).

(74) **Agents:** GREENER, William et al.; Bond, Schoeneck & King, PLLC, 10 Brown Road, Suite 102, Ithaca, New York 14850 (US).

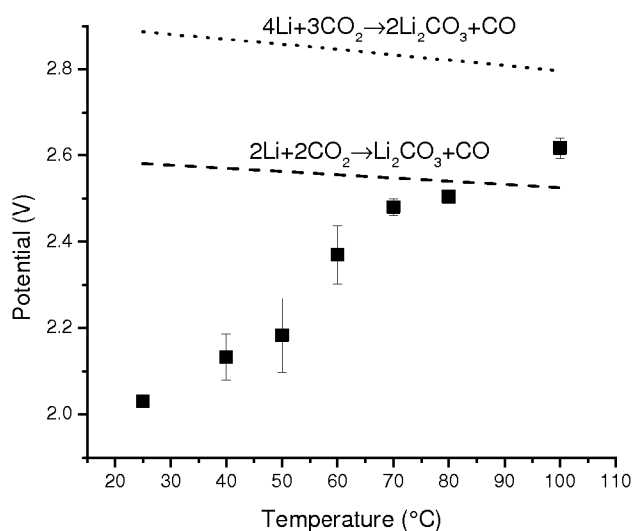
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(54) Title: CARBON DIOXIDE ASSISTED METAL-OXYGEN BATTERY AND RELATED METHOD



(57) **Abstract:** A non-aqueous Na-oxygen battery utilizes a gas mixture of CO_2 and O_2 as fuel. The battery exhibits a comparatively high specific energy of $6500\text{--}7000 \text{ Whkg}^{-1}$ over a range of CO_2 feed compositions. The energy density achieved is higher, by 200 % to 300 %, than obtained with pure oxygen feed. Ex-situ FTIR and XRD analysis confirm Na_2O_2 , $\text{Na}_2\text{C}_2\text{O}_4$ and Na_2CO_3 as discharge products. The $\text{Na-O}_2/\text{CO}_2$ battery provides a promising approach for CO_2 capture and conversion into electrical energy. The $\text{Na-O}_2/\text{CO}_2$ battery may be extended to other metals. In addition, operation of a metal battery fueled at least in-part by carbon dioxide within an optimal temperature range is considered.

CARBON DIOXIDE ASSISTED METAL-OXYGEN BATTERY AND RELATED METHOD

CROSS-REFERENCE TO RELATED APPLICATION

This application is related to, and derives priority from, United States Provisional Patent Application serial number 61/723,022, filed 6 November 2012 and titled Carbon Dioxide Assisted Metal-Oxygen Battery, the contents of which is incorporated herein fully by reference.

STATEMENT OF GOVERNMENT INTEREST

The research undertaken within the context of the embodiments as described herein, and the invention as claimed herein, was supported by the United States Department of Energy through the Energy Materials Center at Cornell University, under award number DE-SC0001086. The United States Government may have rights with respect to the invention as claimed herein.

BACKGROUND

Field of the Invention

Embodiments relate generally to batteries fueled at least in-part by carbon dioxide. More particularly, embodiments relate to enhanced performance batteries fueled at least in-part by carbon dioxide.

Description of the Related Art

Growing interest in electrochemical energy storage for transportation and grid storage has resulted in an intensive search for alternative energy storage technologies that offer specific energies above those achievable ($\sim 200 \text{ Whkg}^{-1}$) with state-of-the-art lithium-ion batteries. More than a decade of research into such storage platforms has helped define the magnitude of the challenges that must be overcome for lithium-ion batteries to achieve specific energies in the 500-700 Whkg^{-1} range. In this context, metal-air batteries and related metal-oxygen batteries are gaining focus because of their exceptionally high specific energies. Among the various metal-air or metal-oxygen batteries, the Li-air (or Li-oxygen) and Zn-air (or Zn-oxygen) technologies have attracted most attention.

Since metal-air or metal-oxygen batteries provide promise due to their high specific energies, desirable are additional metal-air or metal-oxygen batteries and methods for fabrication thereof.

SUMMARY

Embodiments provide a carbon dioxide assisted metal-oxygen battery (i.e., M-O₂/CO₂) and a generalized method for operating a metal battery fueled at least in-part by carbon dioxide.

The carbon dioxide assisted metal-oxygen battery provides a higher energy density output per unit material in comparison with a metal-oxygen battery absent carbon dioxide assistance. The generalized method for operating the metal battery fueled at least in-part by carbon dioxide provides for operation of the at least in-part carbon dioxide fueled metal battery above a threshold temperature below which the at least in-part carbon dioxide fueled metal battery operates inefficiently.

A particular carbon dioxide assisted metal-oxygen battery includes a positive electrode contacted by an oxygen and carbon dioxide containing fuel mixture. This particular carbon dioxide assisted metal-oxygen battery also includes a negative electrode comprising a metal material selected from the group consisting of sodium, magnesium, aluminum, zinc, calcium, copper and iron containing metal materials. This particular carbon dioxide assisted metal-oxygen battery also includes an electrolyte separating the positive electrode and the negative electrode.

Another particular carbon dioxide assisted metal-oxygen battery includes a positive electrode contacted by an oxygen and carbon dioxide containing fuel mixture having an oxygen:carbon dioxide fuel volume ratio from about 10:90 to about 90:10. This other particular carbon dioxide assisted metal-oxygen battery also includes a negative electrode comprising sodium metal. This other particular carbon dioxide assisted metal-oxygen battery also includes an electrolyte separating the positive electrode and the negative electrode.

A particular method for operating a metal battery fueled at least in-part by carbon dioxide includes providing a metal battery comprising: (1) a positive electrode contacted by at least a carbon dioxide containing fuel; (2) a negative electrode comprising a metal material; and (3) an

electrolyte separating the positive electrode and the negative electrode. This particular method also includes operating the battery at a temperature greater than about 40 degrees centigrade.

Another particular method for operating a metal battery fueled at least in-part by carbon dioxide includes providing a battery comprising: (1) a positive electrode contacted by a fuel consisting of carbon dioxide; (2) a negative electrode comprising a metal; and (3) an electrolyte separating the positive electrode and the negative electrode. This other particular method also includes operating the battery at a temperature greater than about 40 degrees centigrade.

In accordance with further disclosure below, a “metal material” as disclosed and claimed herein is in a first instance intended as one of a pure metal and a metal alloy including at least one metal selected from the group consisting of sodium, magnesium, aluminum, zinc, calcium, copper and iron metals. A “metal material” as disclosed and claimed herein is in a second instance also intended to include a metal oxyanion salt including at least one metal selected from the group consisting of sodium, magnesium, aluminum, zinc, calcium, copper and iron metals.

BRIEF DESCRIPTION OF THE DRAWINGS

The objects, features and advantages of the embodiments are understood within the context of the Detailed Description of the Non-Limiting Embodiments, as set forth below. The Detailed Description of the Non-Limiting Embodiments is understood within the context of the accompanying drawings, that form a material part of this disclosure, wherein:

FIG. 1 shows galvanostatic discharge profiles for Na-air cells operated under mixed O_2/CO_2 . (A) ionic liquid electrolyte; (B) tetraglyme electrolyte; (C) variation of capacity with CO_2 concentration; (D) discharge profile for tetraglyme-based Na- O_2/CO_2 cells with a $O_2(37\%)/CO_2(63\%)$ fuel. FIG. 1 also shows AC impedance spectra of Na-air cells at open circuit under: (E) Ar; and (F) O_2/CO_2 atmospheres.

FIG. 2 shows ex-situ TEM micrographs of Super P carbon (A), discharged carbon electrodes harvested from ionic liquid (B) and tetraglyme (C) cells; (D) ex-situ XRD of Super P electrode (a), and electrodes obtained from Na- O_2 ionic liquid cell (b), Na- O_2/CO_2 ionic liquid cell (c) and

Na-O₂/CO₂ tetraglyme cell (d); @, #, \$, % denote graphitic carbon, Na₂O₂, Na₂C₂O₄, Na₂CO₃ phases respectively. Ex-situ FTIR spectra of Super P carbon (Ea, Fa), ionic liquid electrolyte (Eb), tetraglyme electrolyte (Fb), discharged carbon electrodes harvested from: Na-O₂ cells based on ionic liquid (Ec) and tetraglyme (Fc), Na-O₂/CO₂ cells based on ionic liquid (Ed) and tetraglyme (Fd). \$, #, * denote vibrations from Na₂O₂, Na₂C₂O₄, and Na₂CO₃ respectively.

FIG. 3 shows galvanostatic discharge curves for Mg-air cells.

FIG. 4 shows galvanostatic discharge curves of Li-CO₂ cells operated at various temperatures in the range 60°C-100°C at a current density of 0.05mA/cm² to the potential of 2.2V.

FIG. 5 shows a comparison of theoretical equilibrium potential with actual discharge potential. It is evident that the measured cell potential initially approaches the calculated equilibrium potential, but then surpasses it. Based on Tafel theory, the actual discharge potential cannot exceed the theoretical equilibrium potential, implying that the proposed reaction is likely to be only partially correct.

FIG. 6 shows ex-situ XRD results of the cathodes after discharge at (a) 70°C (b) 100°C. Peaks with symbol (*) are the characteristic peaks of Li₂CO₃ and peaks with symbol (#) are from the aluminum substrate.

FIG. 7 shows ex-situ FTIR spectrum of a cathode electrode within a Li-CO₂ battery after discharge at 100°C.

FIG. 8 shows scanning electron micrographs of Super P electrodes after discharging at different temperatures (a) pristine electrode (b) room temperature (c) 40°C (d) 60°C (e) 80°C (f) 100°C.

FIG. 9 shows variation of LiCO₂ cell discharge with temperature: (a) Super P carbon black (SA = ~60 m²/g, PV = 0.3 m³/g) as cathode; (b) high surface area carbon cathode (square symbol: SA= 1020m²/g, PV= 45 m³/g, circle symbol: SA=1300 m²/g, PV=2.2 cm³/g).

FIG. 10 shows galvanostatic discharge curves of (a) Mg-CO₂ battery and (b) Al-CO₂ battery operated at room temperature at a constant current density of 0.05mA/cm².

FIG. 11 shows DEMS analysis of gas phase products for Li-CO₂ battery at (a) room temperature (b) 60°C and (c) cyclic voltammetry of Li-CO₂ battery

FIG. 12 shows a discharge capacity graph for a Li-CO₂ battery.

FIG. 13 shows a graph illustrating variability of discharge capacity as a function electrolyte composition for a Li-CO₂ battery.

FIG. 14 shows a graph illustrating discharge capacity for a rechargeable Na-O₂/CO₂ battery in accordance with the embodiments.

FIG. 15 shows another graph illustrating discharge capacity for a rechargeable Na-O₂/CO₂ battery in accordance with the embodiments.

FIG. 16 shows SEM images of a cathode electrode: (a) pristine; (b) after charge; and (c) after discharge, for a rechargeable Na-O₂/CO₂ battery in accordance with the embodiments.

FIG. 17 shows ex-situ XRD spectra of a cathode electrode: (a) after discharge; and (b) after recharge, for a rechargeable Na-O₂/CO₂ battery in accordance with the embodiments.

DETAILED DESCRIPTION OF THE NON-LIMITING EMBODIMENTS

A.1. Carbon Dioxide Assisted Metal Oxygen (M-O₂/CO₂) Battery

An air battery utilizing Na as anode is particularly attractive because of the high earth abundance, modest cost, and relatively high electrode potential (-2.71 V vs SHE) that may be achieved. Coupled with O₂, Na has the ability to deliver a specific energy of 1600 Whkg⁻¹ (2Na⁺ + O₂ + 2e⁻ → Na₂O₂ at 2.33 V).

CO₂ is a greenhouse gas and has been implicated in global climate change. A variety of chemical and physical methodologies is under development for capturing and sequestering the thousands of metric tons of the gas emitted per annum. A metal-air battery that utilizes a mixed fuel of CO₂ and O₂ provides a potentially novel platform for electrical energy generation and carbon capture.

The embodiments provide in particular, among other carbon dioxide assisted metal oxygen M-O₂/CO₂ battery constructions, a Na-O₂/CO₂ battery operated at room temperature utilizing tetraglyme and an ionic liquid as electrolyte.

2. General Considerations Related to Carbon Dioxide Assisted Metal Oxygen Battery

In general, embodiments provide a carbon dioxide assisted metal-oxygen battery comprising: (1) a positive electrode contacted by an oxygen and carbon dioxide fuel mixture (i.e., which may have an oxygen:carbon dioxide fuel volume ratio from about 10:90 to about 90:10; (2) a negative electrode comprising a metal selected from the group consisting of sodium, magnesium, aluminum, zinc, calcium, copper and iron metals; and (3) an electrolyte separating the positive electrode and the negative electrode. The carbon dioxide assisted metal oxygen battery in accordance with the embodiments may also include a separator also separating the positive electrode and the negative electrode.

More preferably, the M-O₂/CO₂ battery construction in accordance with the embodiments may alternatively use an oxygen:carbon dioxide fuel volume ratio from about 20:80 to about 80:20. More preferably the M-O₂/CO₂ battery construction in accordance with the embodiments uses an oxygen:carbon dioxide fuel volume ratio from about 30:70 to about 70:30.

More specifically, within a M-O₂/CO₂ battery in accordance with the embodiments the positive electrode may comprise a carbon material. Also, more specifically, within a M-O₂/CO₂ battery in accordance with the embodiments the negative electrode may comprise sodium metal. Also more specifically, within a M-O₂/CO₂ battery in accordance with the embodiments the negative electrode may comprise magnesium metal. Also, more specifically, within a M-O₂/CO₂ battery in accordance with the embodiments the electrolyte may comprise an ionic liquid.

With specific respect to the presence of an ionic liquid as an electrolyte, the presence of the ionic liquid as the electrolyte provides that a M-O₂/CO₂ battery in accordance with the embodiments may be rechargeable in a commercially viable fashion. Such rechargeability in the commercially viable fashion includes recharge within the context of a capacity cutoff of 800mAh/g_{carbon}.

Additionally, to optimize performance of a M-O₂/CO₂ battery in accordance with the embodiments the cathode preferably has: (1) a surface area from about 800 to about 1500 m²/g; (2) a pore volume from about 1.5 to about 3 cm³/g; and (3) an average pore size from about 50 to about 100Å.

Additionally, to optimize performance of a M-O₂/CO₂ battery in accordance with the embodiments, the anode may in addition to the foregoing metals also comprise a metal salt selected from the group including but not limited to phosphate salts, fluoroborate salts and other oxyanion salts. Specific examples of such metal salts include, but are not limited to LiCoO₂, LiFePO₄, etc., as mixed polycationic-polyoxyanionic salts.

Additionally to optimize performance of a M-O₂/CO₂ battery in accordance with the embodiments one may also control acidity of an electrolyte. For example a 1:1 ratio of AlCl₃ to imidazolium material provides a balanced acidity of an electrolyte that provides for optimal performance of a Al-O₂/CO₂ battery in accordance with the embodiments.

In that regard, one particular embodiment includes the use of: (1) aluminum as an anode; (2) a mixture of AlCl₃, 1-ethyl-3-methylimidazolium chloride and NaCl with a molar ratio of 2:1:0.1 as an electrolyte; and (3) a porous, conductive cathode in contact with CO₂. In this particular embodiment, a higher molar ratio of AlCl₃ to the imidazolium ionic liquid ensures the acidity of the mixture containing the needed ions of aluminum stripping during battery discharge. NaCl is used as a buffer to ensure continued acidity of the electrolyte. A battery of such architecture demonstrated a discharge capacity of over 7000 mAh/g_{carbon}, an increase of over 4000% compared to the same system without NaCl in the electrolyte. Changing the composition of the electrolyte enables maintaining high discharge capacity of the battery even at relatively higher temperatures. Other alkali metal chloride salts can be used instead of NaCl.

3. Experimental Details of a Na-O₂/CO₂ Battery

The investigated Na-O₂/CO₂ battery configuration is similar to other related battery constructions. An air or oxygen cathode consisted of 90% Super P (TIMCAL) carbon and 10% PVDF binder. Mechanically perforated coin cells were used for electrochemical experiments. 1 M NaClO₄/tetraethylene glycol dimethylether and 0.75M NaCF₃SO₃/1-ethyl-3-methyl imidazolium trifluoromethanesulfonate (IL) were used as electrolytes. The cells were assembled in an argon-filled glove box and fitted into a custom-built stainless steel chamber. Required concentrations of CO₂ and O₂ were premixed in a chamber at 1 atm before introducing the gas feed into the battery chamber. All galvanostatic experiments were performed at 25 °C and at a current density of 70 mA g⁻¹. The porous carbon electrode dimensions were 1.95 cm² with typical carbon loading of 0.76-1.28 mg/cm² and thickness of 5 μm. AC impedance measurements were conducted at frequencies from 100 kHz to 100 mHz at 10 mV bias voltage. For ex-situ TEM, FTIR and XRD analyses, discharged electrodes were vacuum dried and stored in an argon-filled glovebox.

A particular rechargeable Na-O₂/CO₂ battery is similar to the foregoing Na-O₂/CO₂ battery. The cathode is porous carbon. The anode is Na metal. The electrolyte is 1M NaTFSI in propylene carbonate. In the electrolyte was added 10% imidazolium ionic liquid tethered silica particles. See, e.g. publication number WO 2013009731 (application number PCT US2012/046020) or alternatively Lu et al., "Ionic Liquid-Nanoparticle Hybrid Electrolytes and their Application in Secondary Lithium-Metal Batteries," *Adv. Mater.*, 2012, 24, 4430-35, the contents of which is incorporated herein by reference to the extent allowed. The cell has an open cathode so that the gas can go into the cathode and participate in the reaction. The battery can be stably recharged for over 20 cycles at a capacity control of 800mAh/g C. A mechanism of the rechargeability is not necessarily clear.

4. Results and Discussion for the Na-O₂/CO₂ Battery

FIG. 1 reports the galvanostatic discharge profiles of Na-air cells (i.e., M-O₂/CO₂) operated under various concentrations of O₂ and CO₂. FIG. 1A and 1B correspond, respectively, to cells using ionic liquid and tetraglyme-based electrolytes. Under a 100% O₂ environment, the two

varieties of Na-air cells exhibit discharge capacities of 1315 mAhg^{-1} and 1390 mAhg^{-1} , respectively (estimated based on carbon mass). The discharge profiles with the pure O_2 feed show a less well-defined voltage plateau at 2.3 V. This difference might be attributed to subtle differences between the electrolytes and air cathode employed in the present studies since the current rates are similar. The Na-air cells also show low discharge capacities of 183 and 173 mAhg^{-1} under a pure CO_2 environment. Sluggish reaction kinetics between Na^+ ions in solution and CO_2 at room temperature are anticipated, which may explain the latter observation. Remarkably, the discharge capacities of both the ionic liquid and tetraglyme based Na-air cells based on feed streams containing 40% and 63% CO_2 are respectively 3500 and 2882 mAhg^{-1} ; an increase of 2.6 and 2.1 times compared to the Na-100% O_2 case. FIG. 1C reports the relative discharge capacities as a function of CO_2 concentration. The variation in capacity is seen to depend on the chemical composition of the electrolytes, but there is a similar trend for the tetraglyme- and IL-based electrolytes, with the highest discharge capacities observed at intermediate CO_2 compositions. It demonstrates that the specific energy of a Na-air cell can be significantly enhanced, by factors of 2 to 3, by introducing optimized concentrations of CO_2 . The threshold and criticality of capacity enhancement is around 30% and 40-63% of CO_2 respectively.

It is also apparent from FIG. 1A and FIG. 1B that irrespective of electrolyte, there is an improvement in the quality of the discharge voltage profile upon introduction of CO_2 to the cells. A plateau voltage around 2-2.2 V is observed in both cases. FIG. 1D shows discharge profiles obtained from two identical tetraglyme-based Na-air cells operated under $\text{O}_2(37\%)/\text{CO}_2(63\%)$ concentrations. A polarization of $\sim 500 \text{ mV}$ is observed between the cells. To understand the origin of this effect, two identical Na-air cells were assembled and stored separately in Ar and O_2/CO_2 environments. AC impedance spectra of the cells were measured at various time periods at open circuit conditions as shown in FIG. 1E and FIG. 1F. The Nyquist plots show that the semicircles evolve with time in both cases. The results for the Ar-stored Na-air cell suggests that the electrolyte in contact with reactive Na metal forms a stable electrode/electrolyte interface over time. It is also evident from FIG. 1E and FIG. 1F that the Na-air cell stored in O_2/CO_2 exhibit less interfacial stability. As the Na and carbon electrodes were separated by a micrometer thick separator and no gas protective layer covers the Na anode, it is anticipated that O_2/CO_2

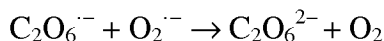
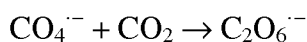
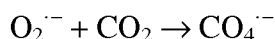
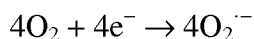
diffuse and react with Na and the reaction products induces an increase in interfacial resistance at the electrode/electrolyte interface. Because a thicker electrode/electrolyte interface is anticipated for the cells stored in the O₂/CO₂ environment, more energy is required for the electrochemically generated Na⁺ ions to migrate to the cathode oxidant, which would cause the observed cell polarization.

To obtain deeper insights into the overall electrochemistry and role of CO₂ in the Na-air cells, the discharged carbon electrodes were harvested and investigated with transmission electron microscopy, x-ray diffraction, and Fourier transform infrared spectroscopy. Ex-situ TEM images (see FIG. 2B and FIG. 2C), indicate that the porous carbon electrodes are filled with discharge products. FIG. 2D shows that additional x-ray diffraction peaks emerge in every case (FIG. 2D b-d). The peaks can be indexed to crystalline phase of Na₂O₂ (ICDD No. 083-0597) in case of electrodes harvested from Na-100% O₂ cells (FIG. 2Db). Remarkably, however, no signature of Na₂O₂ is found in electrodes retrieved from cells using the O₂/CO₂ mixed gas feed. Instead, diffraction peaks corresponding to Na₂CO₃ (ICDD No. 075-6816) and Na₂C₂O₄ (ICDD No. 075-3639) are observed. Additionally, it is apparent that while Na₂CO₃ and Na₂C₂O₄ coexist in discharged electrodes from the tetraglyme based Na-O₂/CO₂ cells (FIG. 2Dd), Na₂C₂O₄ is the dominant phase in electrodes harvested from cells using the ionic liquid electrolyte (FIG. 2Dc). Ex-situ FTIR performed on the discharged electrodes support these observations (FIG. 2E and FIG. 2F). In addition to the vibration spectral signature of the pure electrolytes, peaks at 1652 cm⁻¹ and 877 cm⁻¹ (FIG. 2Ec and FIG. 2Fc, marked by \$) can be identified and assigned to vibrations from Na₂O₂. Peaks at 1632 cm⁻¹ and 775 cm⁻¹ (FIG. 2Ed, marked by #) respectively correspond to antisymmetric stretching and in plane deformation frequencies of O—C—O bonds of oxalates. Similarly, peaks at 1426 cm⁻¹ and 879 cm⁻¹ (FIG. 2Fd, marked by *) respectively correspond to the symmetric and antisymmetric stretching frequencies of O—C=O bonds of carbonates.

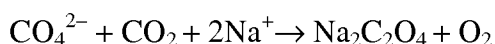
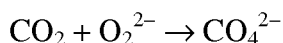
The XRD and FTIR results suggest that the following electrochemical reaction may occur to form Na₂O₂ in the cells that employ pure O₂: $O_2 + 2e^- + 2Na^+ \rightarrow Na_2O_2$. The processes by which Na₂CO₃ and Na₂C₂O₄ are formed in cells employing a O₂/CO₂ mixed gas as feed are evidently more complex. Electrochemical reduction of O₂ and CO₂ are known to involve a range

of complicated elementary reactions and also depends on the solvent and electrode material. It should be noted nonetheless that the fact that only $\text{Na}_2\text{C}_2\text{O}_4$ forms in ionic liquid based electrolytes, whereas both Na_2CO_3 and $\text{Na}_2\text{C}_2\text{O}_4$ coexist in tetraglyme cells indicates that the reactions are not hopelessly complex. Various research groups have reported on the electrochemical reduction of O_2 and CO_2 . Based on the reported results and the observations above, proposed are the following reaction mechanisms for the $\text{Na-O}_2/\text{CO}_2$ cell.

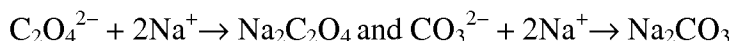
Mechanism 1:



Mechanism 2: The O_2 electroreduction reaction in aprotic organic solvents is as follows. (i) $\text{O}_2 + \text{e}^- \rightarrow \text{O}_2^{\cdot-}$ and (ii) $\text{O}_2 + 2\text{e}^- \rightarrow \text{O}_2^{2-}$. Since $\text{Na}_2\text{C}_2\text{O}_4$ is also a discharge product, the following reactions are also clearly possible:



Mechanism 3: The CO_2 electroreduction reaction in aprotic organic solvents is as follows. (i) $2\text{CO}_2 + 2\text{e}^- \rightarrow \text{C}_2\text{O}_4^{2-}$ and (ii) $2\text{CO}_2 + 2\text{e}^- \rightarrow \text{CO}_3^{2-} + \text{CO}$. Since Na-100% CO_2 cells also show some capacity, a direct reaction with dissolved CO_2 must also be possible. One may therefore propose the following reactions:



Considering a typical discharge voltage plateau at $\sim 2\text{ V}$ in $\text{Na-O}_2/\text{CO}_2$ cells and based on the above mechanisms, it appears mechanism 1 and 2 are most probable since mechanism 3 would lead to a cell voltage of $\sim 200\text{ mV}$, with mechanism 2 dominating in the IL-based electrolyte.

The same ideas outlined above would lead one to expect that electrochemical properties of non-aqueous primary metal-air cells based on other earth-abundant metals, e.g. Mg, may also be enhanced by introduction of CO₂. To evaluate this idea, assembled was a non-aqueous Mg-air cell as a proof of concept. 1M Mg(ClO₄)₂-propylene carbonate was used as electrolyte. As illustrated in FIG. 3, the Mg-air cell shows a discharge voltage plateau of ~ 0.9 V and close to a factor of 250% enhancement in specific energy with introduction of 50% CO₂.

With respect to performance characteristics of a rechargeable Na-O₂/CO₂ battery as described above, charge and discharge profiles were measured at: (1) a current density of 200 mA/g_{carbon}; (2) a capacity cutoff of 800 mAh/g_{carbon}; and (3) a voltage cutoff of 1.7 V for discharge and 5V for charge. Particular charge and discharge capacity profiles are illustrated in FIG. 14, where for both charge and discharge little difference is seen between 1 (bottom curve) and 20 (top curve) cycles.

Additional data is shown in FIG. 15, which illustrates flat and stable capacity (triangle) and charge potential (diamond), with some deterioration of discharge potential (square) above 25 charge and discharge cycles.

Further, FIG. 16 shows SEM images of a cathode electrode within the Na-O₂/CO₂ battery: (a) as pristine; (b) after discharge; and (c) after charge. As is illustrated in FIG. 16(a), the pristine cathode is an aggregation of carbon particles. As is illustrated in FIG. 16(b), after discharge the interparticle space within the cathode electrode is filled by the discharge product. As is illustrated in FIG. 16(c), after charge the carbon particles are more separate and the discharge product disappears to some extent. The foregoing observations, in particular, are consistent with the Na-O₂/CO₂ battery being rechargeable.

Finally, FIG. 17 shows ex-situ XRD spectra of a cathode electrode within the Na-O₂/CO₂ battery: (a) after discharge; and (b) after recharge. As is illustrated in FIG. 17(a) characteristic peaks of NaHCO₃ discharge product at about 30 and 35 degrees 2 θ are apparent. However, after recharge those discharge product peaks largely disappear. This observation too is consistent with

rechargeability of the Na-O₂/CO₂ battery. The remaining peaks at about 39 and 45 degrees 2 θ are indicative of an aluminum substrate.

5. Conclusions for the Na-O₂/CO₂ Battery Configuration

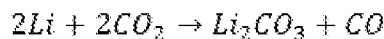
In summary, investigated was a primary non-aqueous Na-O₂/CO₂ battery as a dual platform for converting a CO₂-rich gas stream to electrical energy and for capturing the CO₂. The Na-air battery shows enhancements of 200 to 300% when a mixed with CO₂/O₂ gas with high CO₂ content is used as fuel. Preliminary postmortem structural analysis indicates that Na₂CO₃ and Na₂C₂O₄ are formed. One may further show that metal-air batteries based on other, earth-abundant metals may also benefit from CO₂-enriched fuels. Also investigated was a rechargeable non-aqueous Na-O₂/CO₂ battery.

B.1. Temperature Effects of Metal Batteries Fueled at Least in-Part by Carbon Dioxide

Mankind's total energy consumption is currently 14TW and is projected to roughly triple by the year of 2050. In 2009 it was estimated that close to 83% of current energy needs are met by combustion of fossil fuels (coal, natural gas, and petroleum products), all of which introduce large amounts of carbon dioxide into the environment. Carbon dioxide is now understood to be one of the leading greenhouse gases. The emissions are on the order of thousands of metric tons per annum.

Recently the lithium-air battery has become the subject of intensive investigation worldwide as a promising technology for meeting growing energy demands for transportation. Interest in the lithium air battery is fueled by its exceptionally high theoretical specific energy (11680 Wh/kg Li), which is around 90% that of commercial grade gasoline (13000 Wh/kg). The high energy density of Li-air battery comes from the fact that the cathode-oxygen harvested from the ambient air is not a part of the battery cell. Therefore, the discharge process is not limited by the consumption of the cathode material.

The chemical reaction between lithium metal and CO₂ gas has been known for a very long time. Lithium metal can react with CO₂ gas to form lithium oxalate at room temperature. At high temperature, lithium oxalate can decompose to form lithium carbonate and carbon monoxide gas:



2. General Considerations for Thermal Effects on Metal Batteries Fueled at Least in-Part by CO₂

In accordance with this aspect of a battery in accordance with the embodiments, the embodiments provide a method comprising: (1) providing a battery comprising: (a) a positive electrode contacted by at least a carbon dioxide containing fuel; (b) a negative electrode comprising a metal; and (c) an electrolyte separating the positive electrode and the negative electrode. The method also provides for (2) operating the battery at a temperature greater than about 30 degrees centigrade.

A particular battery whose performance may be enhanced in accordance with the embodiments is a carbon dioxide assisted metal oxygen battery M-O₂/CO₂ otherwise in accordance with the embodiments as described above. In addition, another battery whose performance may be enhanced in accordance with the embodiments is a metal carbon dioxide battery.

3. Experimental Details for Li-CO₂ Battery Configuration

The investigated Li-CO₂ battery configuration is generally similar to the Na-O₂/CO₂ cell described above. In particular, coin-type cells mechanically perforated on the cathode side were used for electrochemical experiments. The cathode material was created by blending conductive carbons with varying porosities, pore size distributions, and surface area with a PVDF polymer binder in NMP. A fixed mass ratio of carbon to PVDF of 9:1 was used for all of the systems studied. The NMP slurry was cast on an aluminum mesh substrate (diameter 1.6 cm) and dried. An electrolyte comprised of 1M LiTFSI in the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide ([bmim][Tf₂N]) was used for the Li-CO₂ cells. The Mg-CO₂ cells employed 1M Mg(ClO₄)₂ in propylene carbonate (PC) and the Al-CO₂ cells used AlCl₃ dissolved in 1-ethyl-3-methylimidazolium chloride ([EMIm]Cl) in a 1.1:1 molar ratio. The cells were assembled in an argon filled glove box. The assembled cells were then sealed into a customized stainless steel chamber filled with CO₂ gas (1atm pressure) and connected to the battery test stand.

4. Results and Discussion for Li-CO₂ Battery

FIG. 4 shows the galvanostatic discharge curves of Li-CO₂ batteries at temperatures in the range of 60°C to 100°C at a fixed current density of 0.05mA/cm² and final potential of 2V. It is apparent from the FIG. 4 that the discharge potential increases with temperature. FIG. 5 shows that the increase is not monotonic, but rather there is a “thermal trigger” region in the 40°C to 60°C temperature range where the largest changes in the cell discharge potential are observed. It is possible to estimate the Li-CO₂ cell potential theoretically from knowledge of the electrochemical reactions underway using the formula $E = -\Delta G/zF$. ΔG is the change in Gibbs free energy, z the number of electrons transferred per mole of product, and F the Faraday constant. If one assumes, for example, that the simplest known reaction between Li and CO₂ $2Li + 2CO_2 \rightarrow Li_2CO_3 + CO$, the cell potential is estimated based on thermodynamic data and shown in FIG. 5 dashed line. It is evident that the measured cell potential initially approaches the calculated equilibrium potential, but then surpasses it. Based on Tafel theory, the actual discharge potential cannot exceed the theoretical equilibrium potential, implying that the proposed reaction is likely only partially correct. Additional insight into the electrochemical reaction can be obtained from analysis of the gas phase composition in a Li-CO₂ cell using differential electrochemical mass spectrometry (DEMS) as illustrated in FIG. 11. These measurements indicate that CO is not a significant reaction product, which provides further evidence against the proposed cell reaction. It is known that CO disproportionates in an $2CO \rightarrow CO_2 + C$, but under normal conditions, the reaction rate is slow. This process is relevant in the present case because it provides a natural mechanism to explain the absence of CO in the gas phase product. Its consideration leads to the overall reaction, $4Li + 3CO_2 \rightarrow 2Li_2CO_3 + C$, where lithium carbonate is again a principal discharge product. The cell potential estimate based on this reaction is provided in FIG. 5 as the dotted line. It is apparent that the measured cell discharged potentials at elevated temperature is consistently lower than the equilibrium potentials estimated for the two proposed mechanisms, implying that this reaction could be relevant for understanding the electrochemistry of the Li-CO₂ cell. Li₂CO₃ is also evidently the principle solid discharge product for both reaction mechanisms hypothesized for the Li-CO₂ battery. This expectation is directly confirmed by ex-situ x-ray powder diffraction (XRD) (FIG. 6) and FTIR analysis (FIG. 7) conducted on the cathode following discharge. These measurements clearly show that Li₂CO₃ is an important, perhaps even the important component of the Li-CO₂ battery discharge product.

FIG. 8 are SEM images of the carbon cathode in the Li-CO₂ cell following discharge at varying temperatures. It is clearly apparent from the figure that as the operating temperature is increased, a progressively thicker film of the Li₂CO₃ product accumulates on the carbon cathode, eventually covering it with a contiguous-polymer like coating.

Commensurate with the increases in the cell discharge potential, FIG. 4 also clearly shows that the discharge capacity of the Li-CO₂ cells rise with temperature. This result is illustrated more clearly in FIG. 9, where the discharge capacity is reported as a function of temperature for Li-CO₂ cells utilizing porous carbon anodes with differing surface areas and pore volumes. The figure shows that irrespective of the cathode surface area and pore volume, moderate increases in the cell temperature consistently produce higher discharge capacities. However, the rate of increase is considerably lower for cells based on high surface area cathodes.

It is also noteworthy from the results in FIG. 9 that, as is the case for the cell potential, the lowest surface area super P-based carbon cathode shows a thermal triggering effect in its performance. In particular, at temperatures between 40 °C and 60 °C, the discharge capacity of Li-CO₂ cells gassed on these cathodes rise rapidly. The discharge capacity of the Li-CO₂ cell at 40 °C increases by a factor of around seven. Thus, the embodiments consider operation of a battery at temperatures of at least about (or greater than about) 40 °C, 60 °C, 80 °C or 100 °C, as well as any intervening intervals of temperature within the context of the foregoing temperature limitations.

In closing, one may point out that the behaviors reported here are not unique to metal-CO₂ cells based on metallic lithium anodes. Similar observations have been made for cells based on magnesium (Mg), aluminum (Al), and sodium (Na) anodes (FIG. 10). All of these materials are advantageous for their greater earth-abundance and lower cost than Li. As in the case of Li-CO₂, however, these cells manifest low discharge capacities at room temperature, but these values can be made substantially larger using a combination of moderately higher cell operating temperatures and cathode materials with higher surface areas and pore volumes. The cell discharge potentials are also commensurately (for electrochemical reactions that produce the

appropriate metal carbonates).

5. Experimental Details, Results and Discussion for Al-CO₂ Battery

In addition to the foregoing Li-CO₂ battery an Al-CO₂ battery was also fabricated. The Al-CO₂ battery also used: (1) an Al anode; (2) a porous cathode allowing the dissolution of CO₂ into an electrolyte (and being made by casting Ketjenblack carbon with PVDF binder (80:20) on a stainless steel current collector); and (3) the electrolyte that consisted of aluminum chloride, 1-ethyl-3-methylimidazolium chloride and sodium chloride in a molar ratio of 2:1:0.2.

FIG. 12 shows a galvanic discharge capacity of such a battery. FIG. 13 shows how changing the electrolyte composition of the foregoing battery with respect to sodium chloride molar ratio allows for maintaining a relatively high discharge of such an Al-CO₂ battery.

6. Conclusion

In summary, investigated was a primary Li-CO₂ battery as a platform for capturing CO₂ and producing electrical energy. The discharge capacity of Li-CO₂ battery showed an enhancement of about 200 times at 100°C compared with the same battery operated at low temperature (i.e., 30°C). Based on preliminary ex-situ analyses, Li₂CO₃ was concluded as an important component of the discharge products. Besides lithium, other more abundant metals like Na, Mg and Al also show promise as the anode material of a metal-CO₂ battery.

All references, including publications, patent applications, and patents cited herein are hereby incorporated by reference in their entireties to the extent allowed, and as if each reference was individually and specifically indicated to be incorporated by reference and was set forth in its entirety herein.

The use of the terms "a" and "an" and "the" and similar referents in the context of describing the invention (especially in the context of the following claims) is to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The terms "comprising," "having," "including," and "containing" are to be construed as open-ended terms (i.e., meaning "including, but not limited to,") unless otherwise noted. The term

“connected” is to be construed as partly or wholly contained within, attached to, or joined together, even if there is something intervening.

The recitation of ranges of values herein is merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it was individually recited herein.

All methods described herein may be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., "such as") provided herein, is intended merely to better illuminate embodiments of the invention and does not impose a limitation on the scope of the invention unless otherwise claimed.

No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention.

It will be apparent to those skilled in the art that various modifications and variations can be made to the present invention without departing from the spirit and scope of the invention. There is no intention to limit the invention to the specific form or forms disclosed, but on the contrary, the intention is to cover all modifications, alternative constructions, and equivalents falling within the spirit and scope of the invention, as defined in the appended claims. Thus, it is intended that the present invention cover the modifications and variations of this invention provided they come within the scope of the appended claims and their equivalents.

CLAIMS

What is claimed is:

1. A battery comprising:

a positive electrode contacted by an oxygen and carbon dioxide containing fuel mixture;
a negative electrode comprising a metal material selected from the group consisting of sodium, magnesium, aluminum, zinc, calcium, copper and iron containing metal materials; and
an electrolyte separating the positive electrode and the negative electrode.

2. The battery of claim 1 wherein the oxygen and carbon dioxide containing fuel mixture has an oxygen:carbon dioxide fuel volume ratio from about 10:90 to about 90:10.

3. The battery of claim 1 wherein the oxygen and carbon dioxide containing fuel mixture has an oxygen:carbon dioxide fuel volume ratio from about 20:80 to about 80:20.

4. The battery of claim 1 wherein the oxygen and carbon dioxide containing fuel mixture has an oxygen:carbon dioxide fuel volume ratio from about 30:70 to about 70:30.

5. The battery of claim 1 further comprising a separator also separating the positive electrode and the negative electrode.

6. The battery of claim 1 wherein the positive electrode comprises a carbon material.

7. The battery of claim 1 wherein the negative electrode comprises sodium metal.

8. The battery of claim 1 wherein the metal material comprises one of a pure metal and a metal alloy including at least one metal selected from the group consisting of sodium, magnesium, aluminum, zinc, calcium, copper and iron metals.

9. The battery of claim 1 wherein the metal material comprises a metal oxyanion salt including at least one metal selected from the group consisting of sodium, magnesium, aluminum, zinc, calcium, copper and iron metals.
10. The battery of claim 1 wherein the electrolyte comprises an ionic liquid.
11. The battery of claim 10 wherein the battery is rechargeable.
12. The battery of claim 1 wherein the battery is not rechargeable.
13. The battery of claim 1 wherein the cathode has:
 - a surface area from about 800 to about 1500 m²/g;
 - a pore volume from about 1.5 to about 3 cm³/g; and
 - an average pore size from about 50 to about 100Å.
14. A battery comprising:
 - a positive electrode contacted by an oxygen and carbon dioxide containing fuel mixture having an oxygen:carbon dioxide fuel volume ratio from about 10:90 to about 90:10;
 - a negative electrode comprising a sodium metal; and
 - an electrolyte separating the positive electrode and the negative electrode.
15. A method comprising:
 - providing a battery comprising:
 - a positive electrode contacted by at least a carbon dioxide containing fuel;
 - a negative electrode comprising a metal material; and
 - an electrolyte separating the positive electrode and the negative electrode; and
 - operating the battery at a temperature greater than about 40 degrees centigrade.
16. The method of claim 15 wherein the metal material comprises one of a pure metal and a

metal alloy that includes at least one metal selected from the group consisting of lithium, aluminum, sodium and magnesium.

17. The method of claim 15 wherein the metal material comprises a metal oxyanion salt that includes at least one metal selected from the group consisting of lithium, aluminum, sodium and magnesium.

18. The method of claim 15 wherein the battery is selected from the group consisting of a carbon dioxide fueled metal battery and a carbon dioxide assisted metal oxygen battery.

19. A method comprising:

providing a battery comprising:

a positive electrode contacted by a fuel consisting of carbon dioxide;

a negative electrode comprising a metal material; and

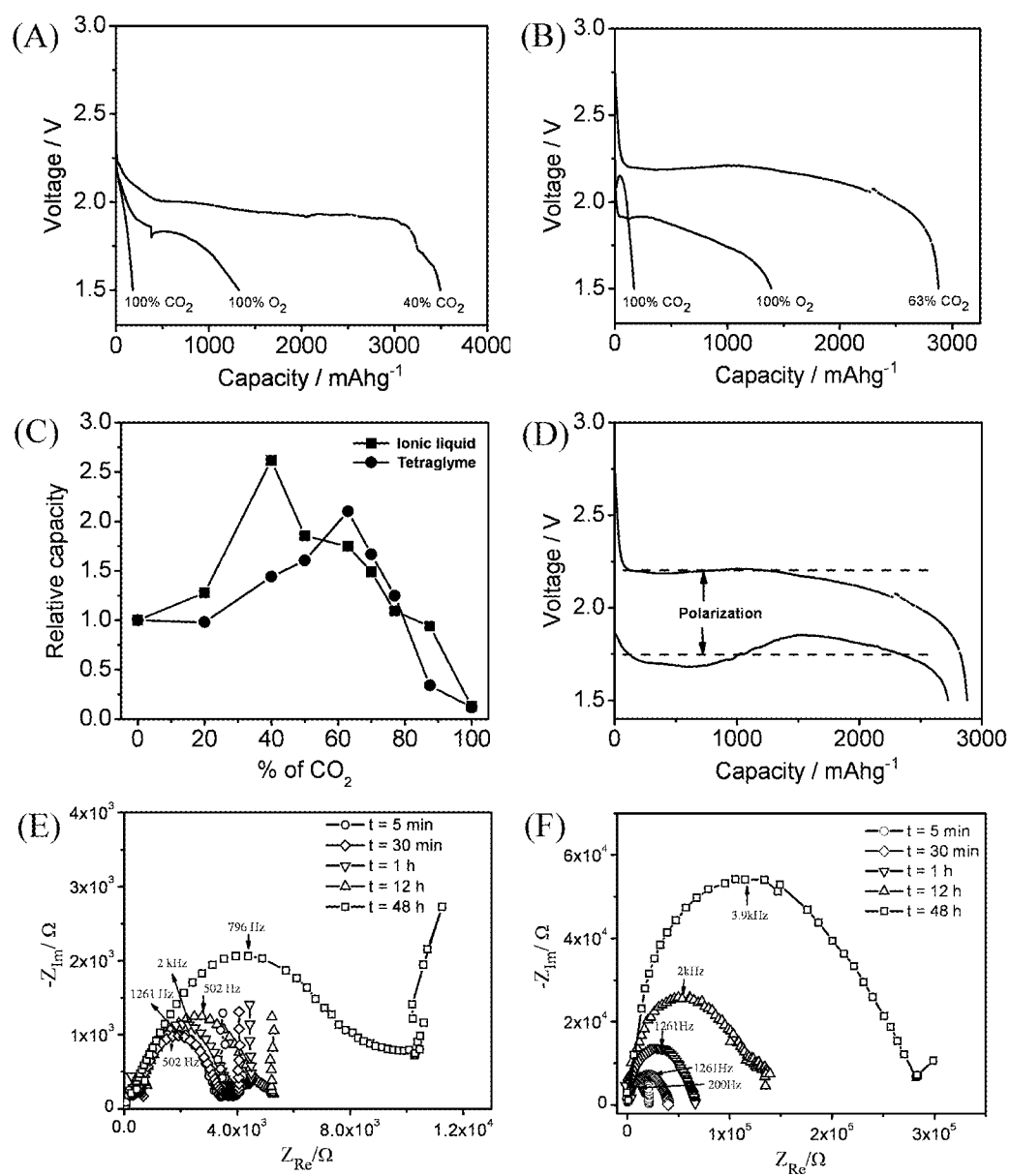
an electrolyte separating the positive electrode and the negative electrode; and

operating the battery at a temperature greater than about 40 degrees centigrade.

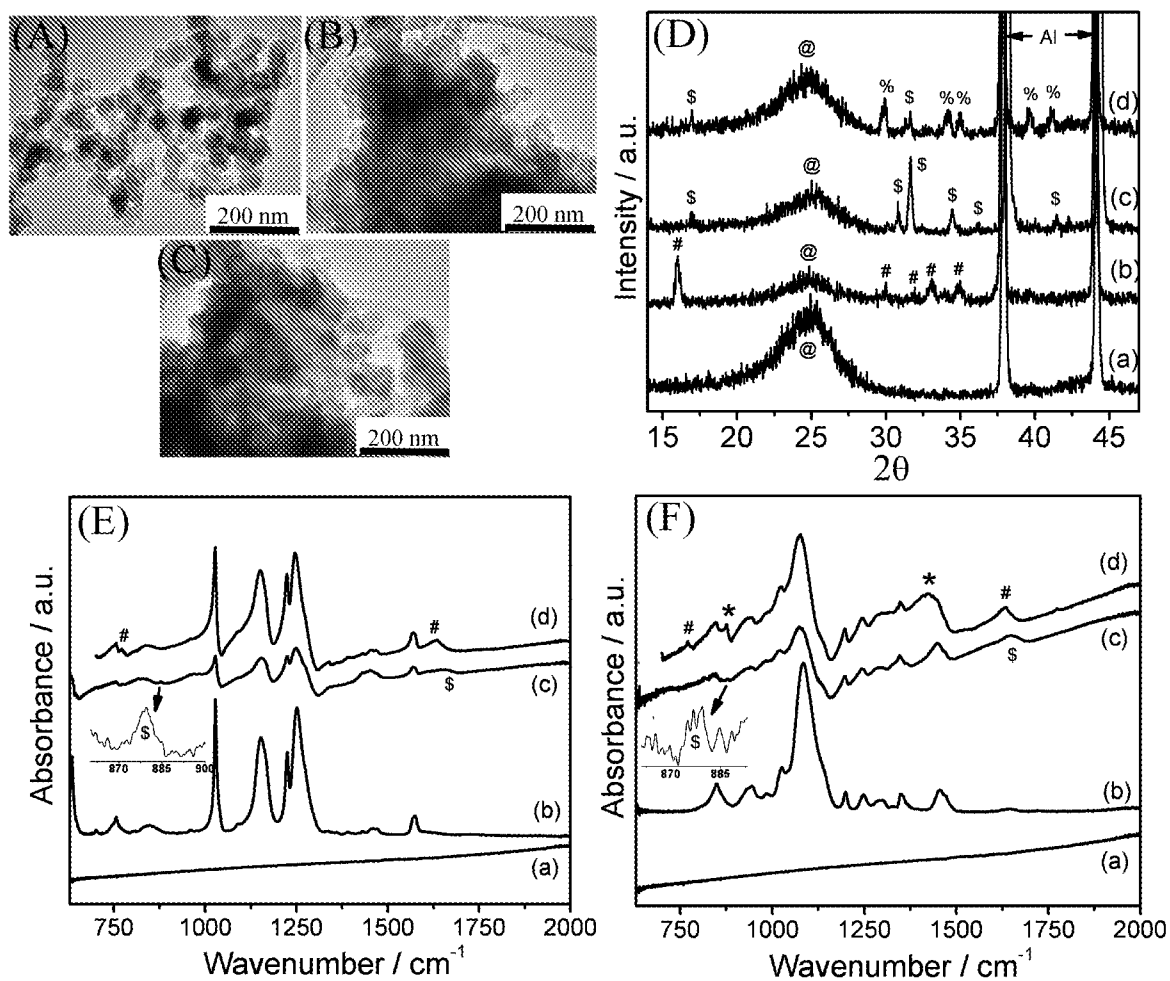
20. The method of claim 18 wherein the negative electrode comprises one of a pure metal and a metal alloy including at least one metal selected from the group consisting of lithium, sodium, magnesium and aluminum metals.

21. The method of claim 18 wherein the negative electrode comprises a metal oxyanion salt including at least one metal selected from the group consisting of lithium, sodium, magnesium and aluminum metals.

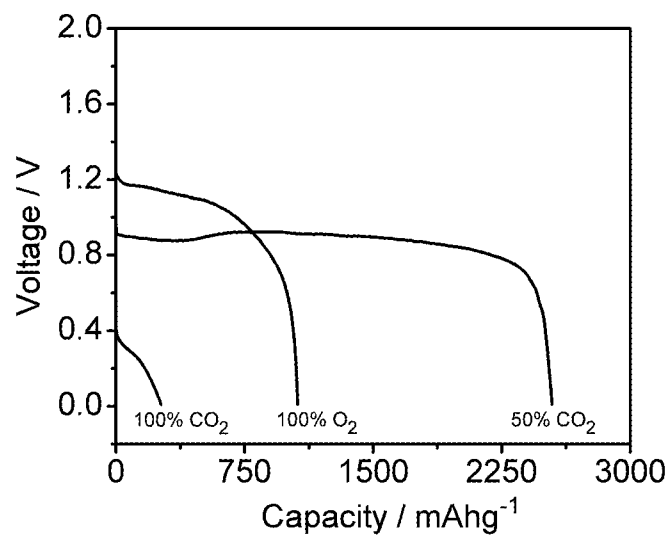
22. The method of claim 18 wherein the battery is operated at a temperature from about 40 to about 60 degrees.



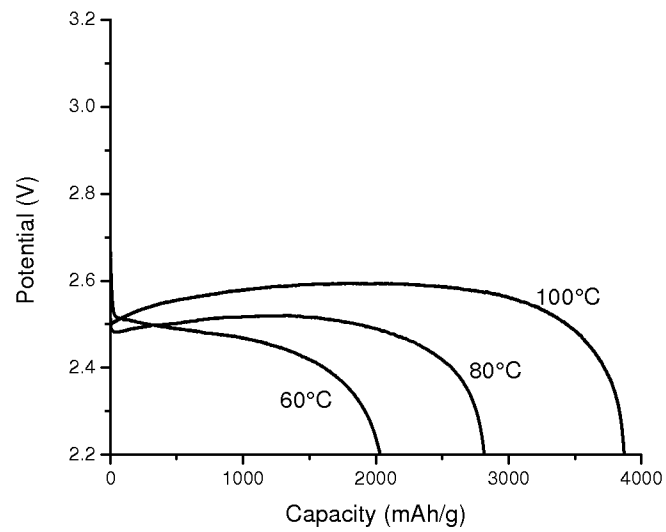
G. 1



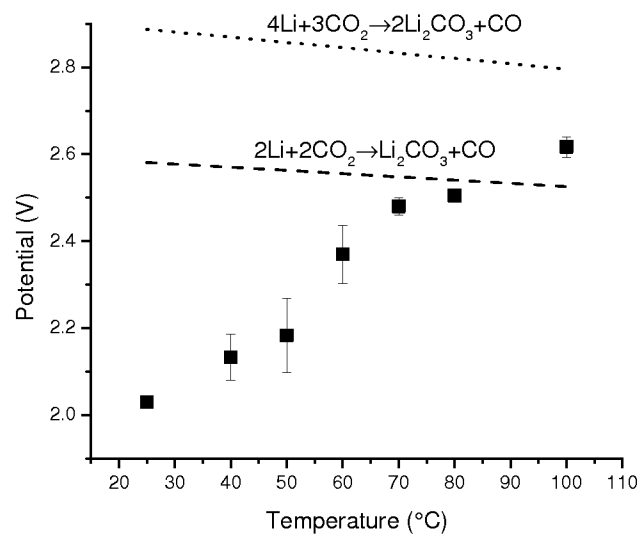
G. 2



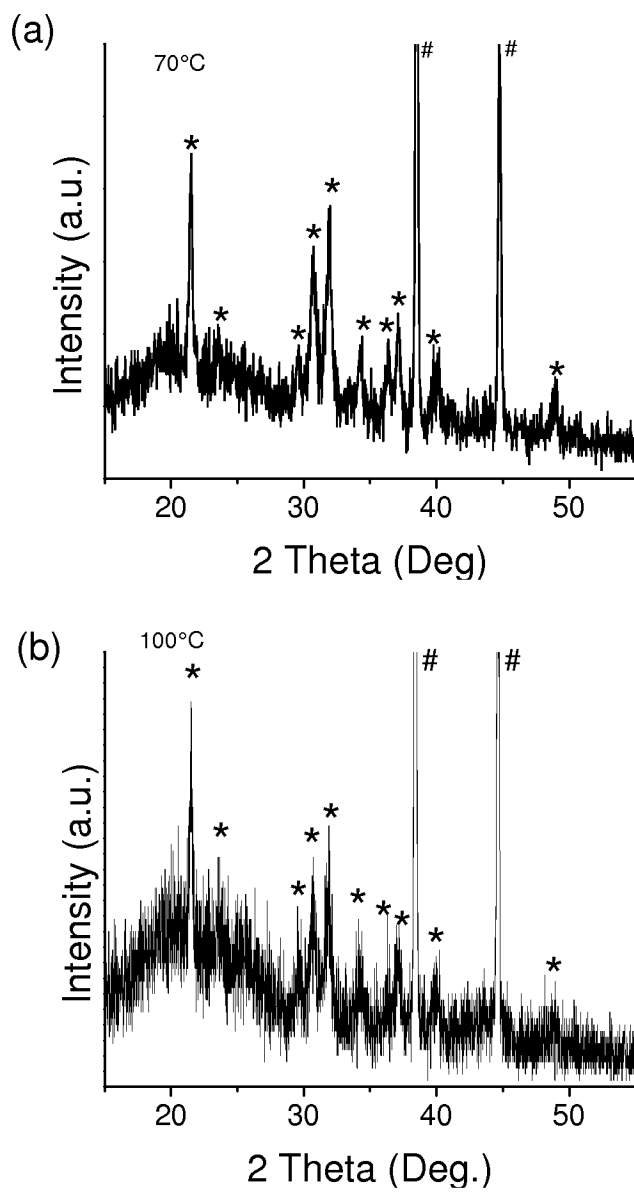
G. 3

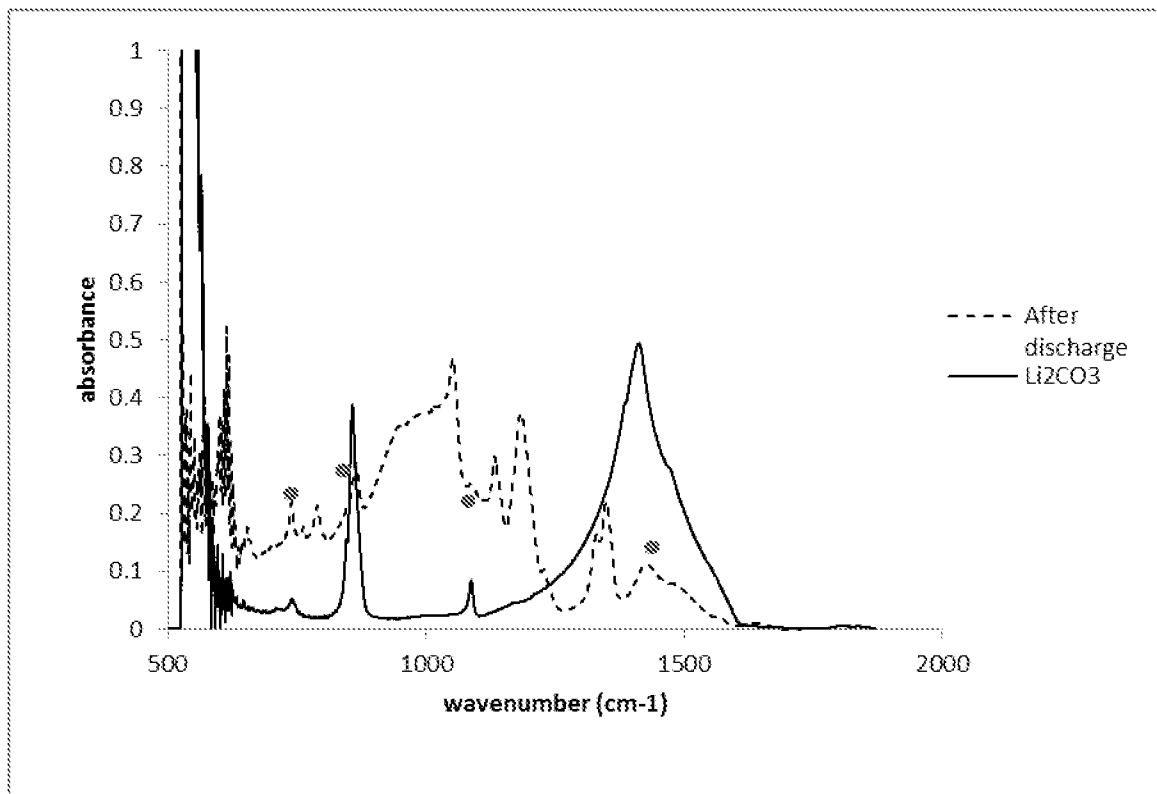


G. 4

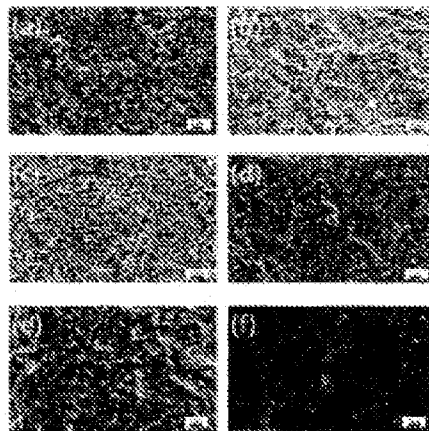


G. 5

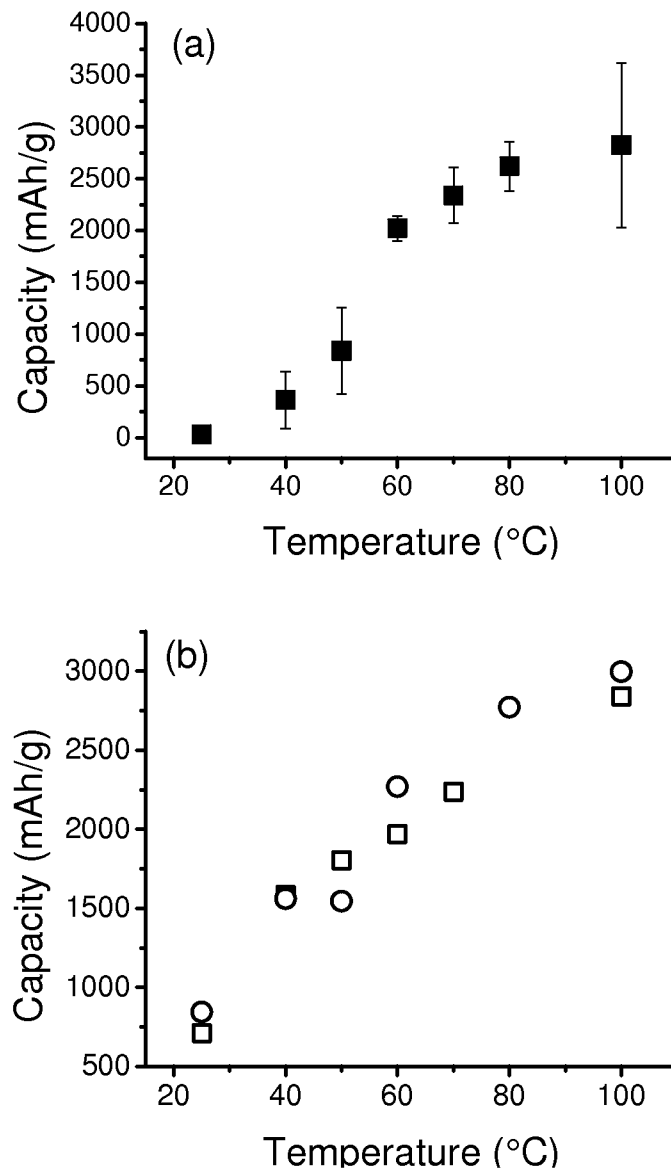


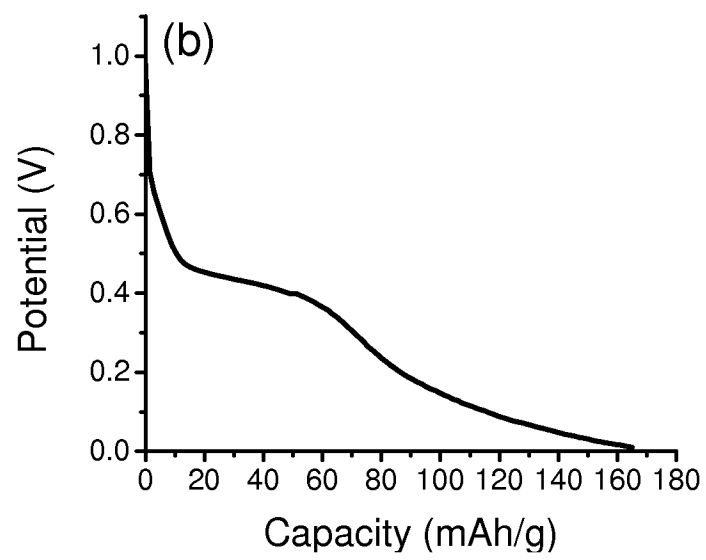
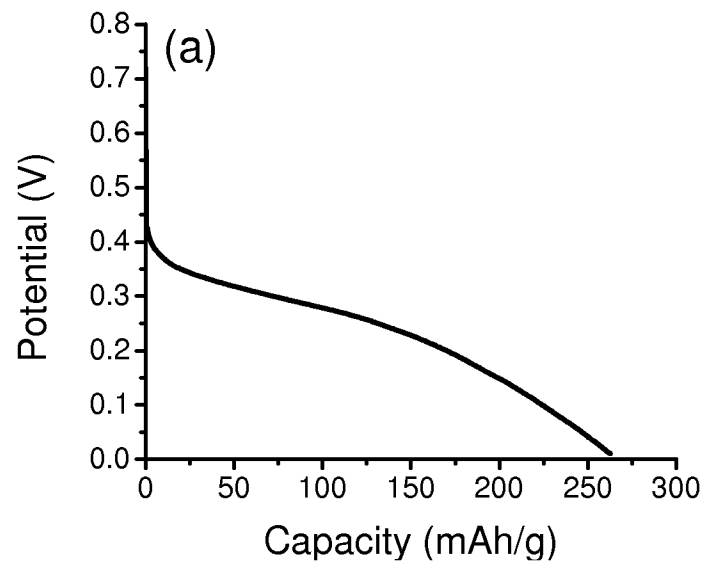


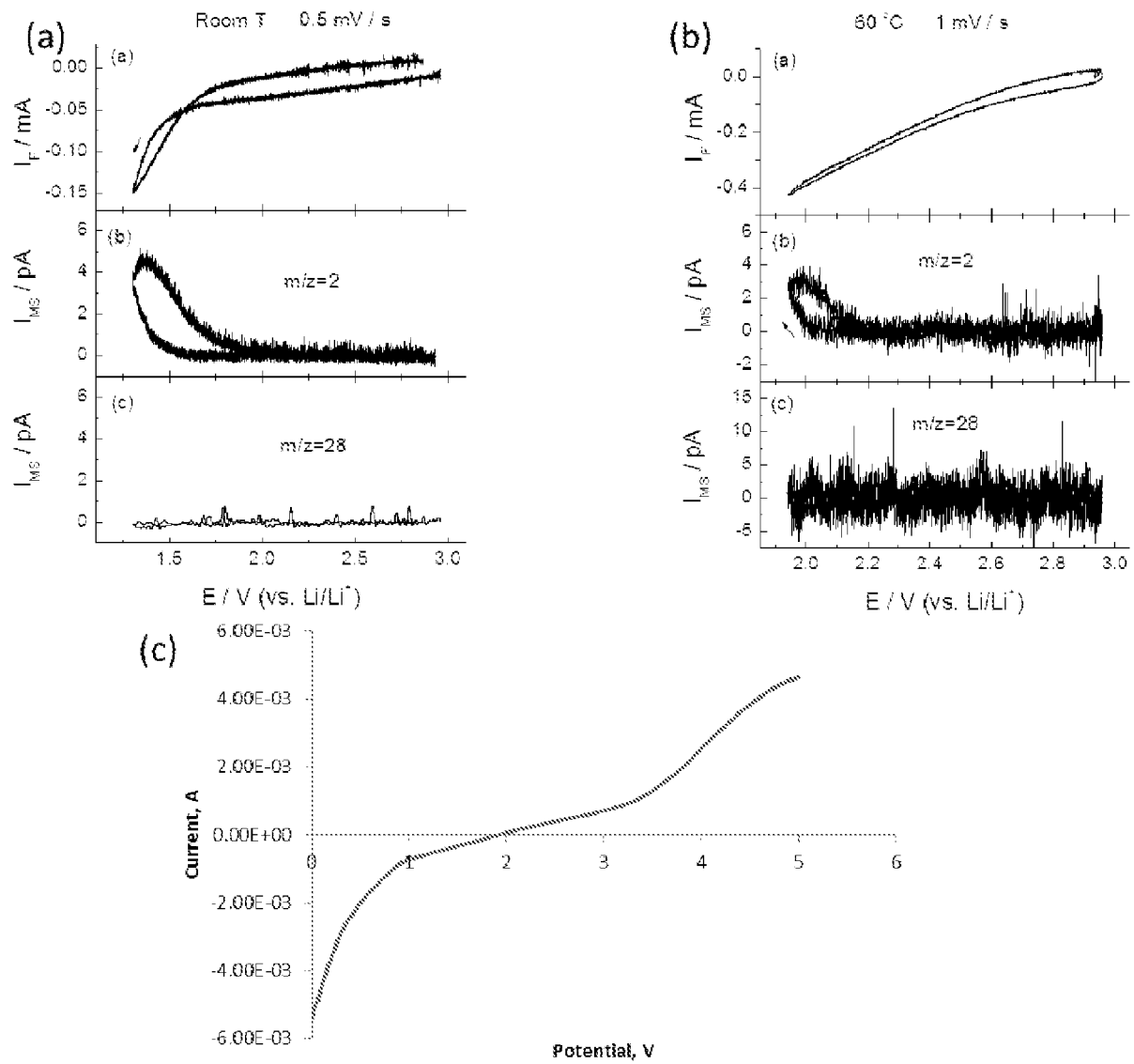
G. 7

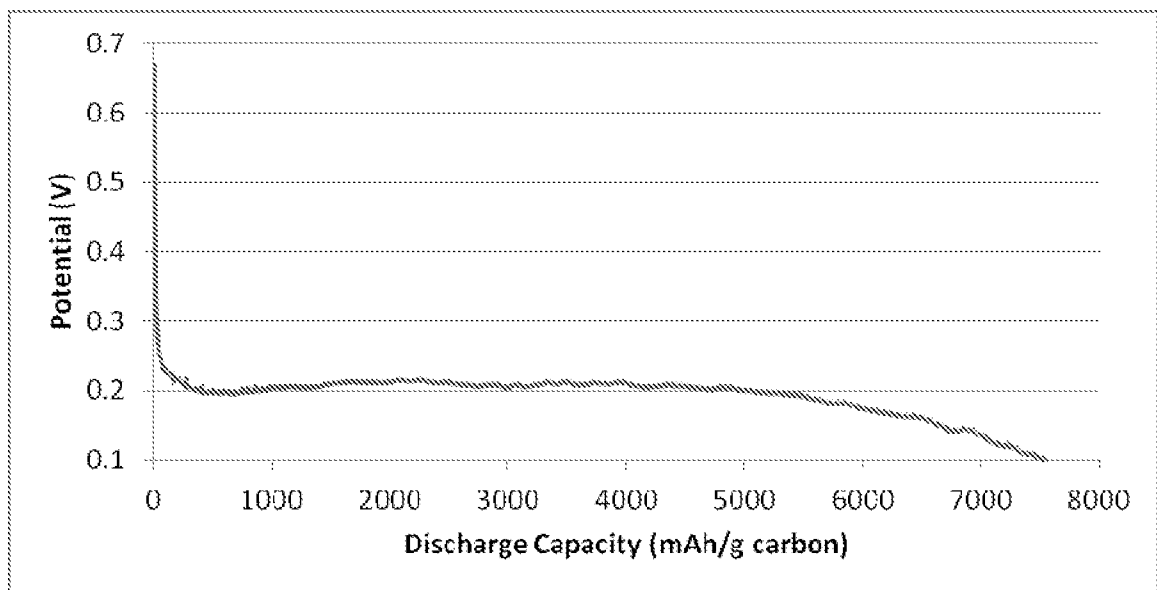


G. 8

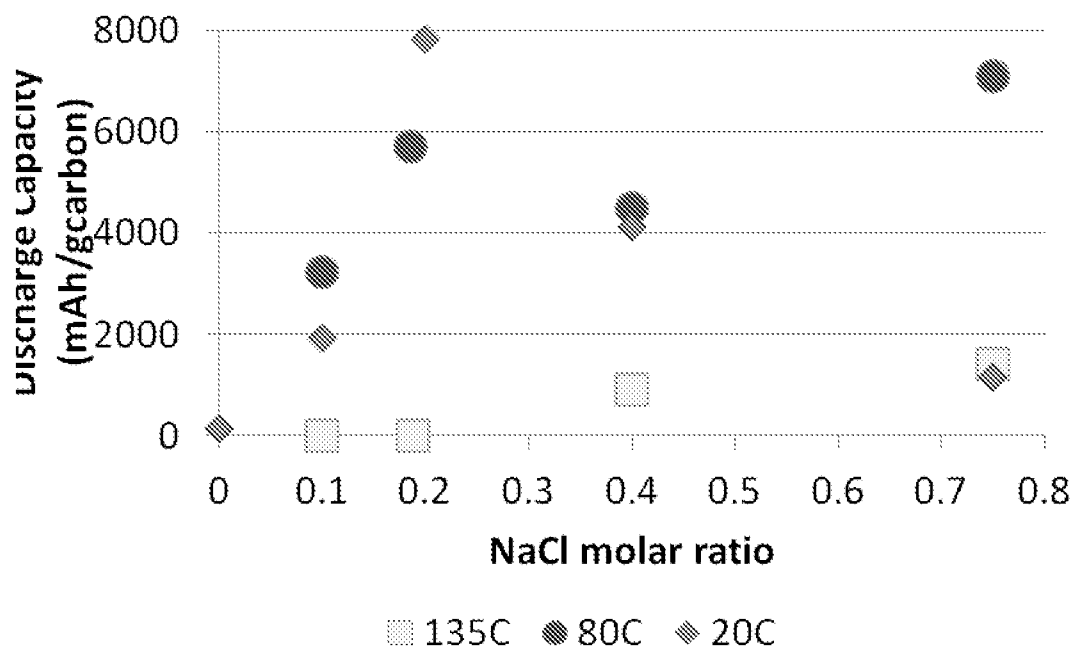




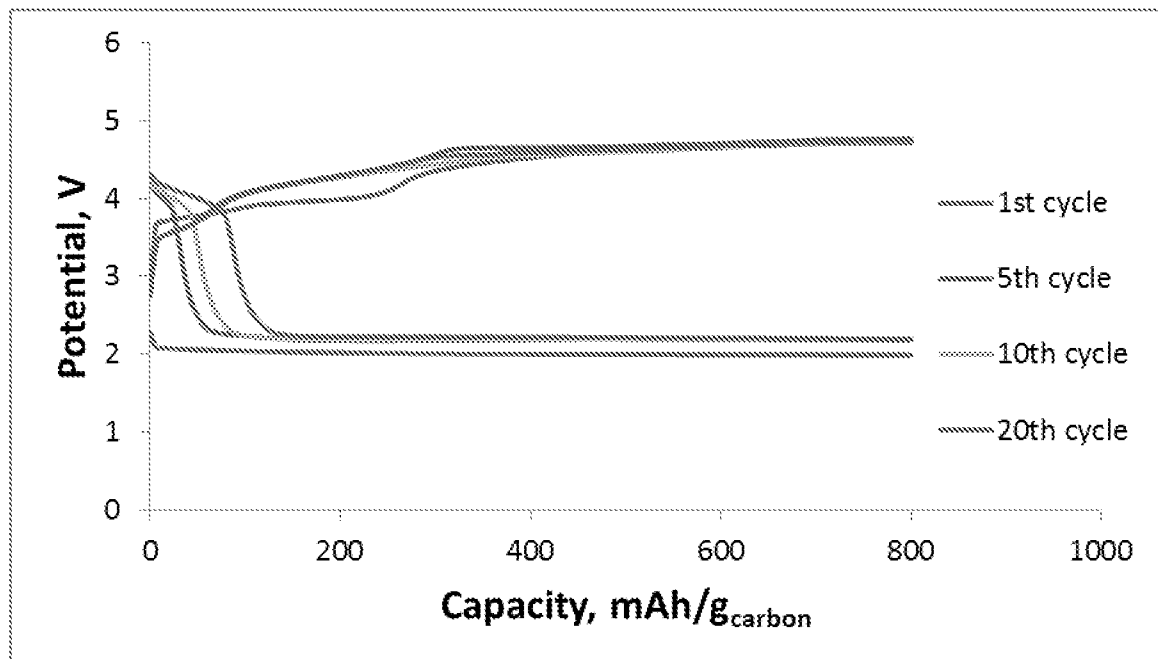




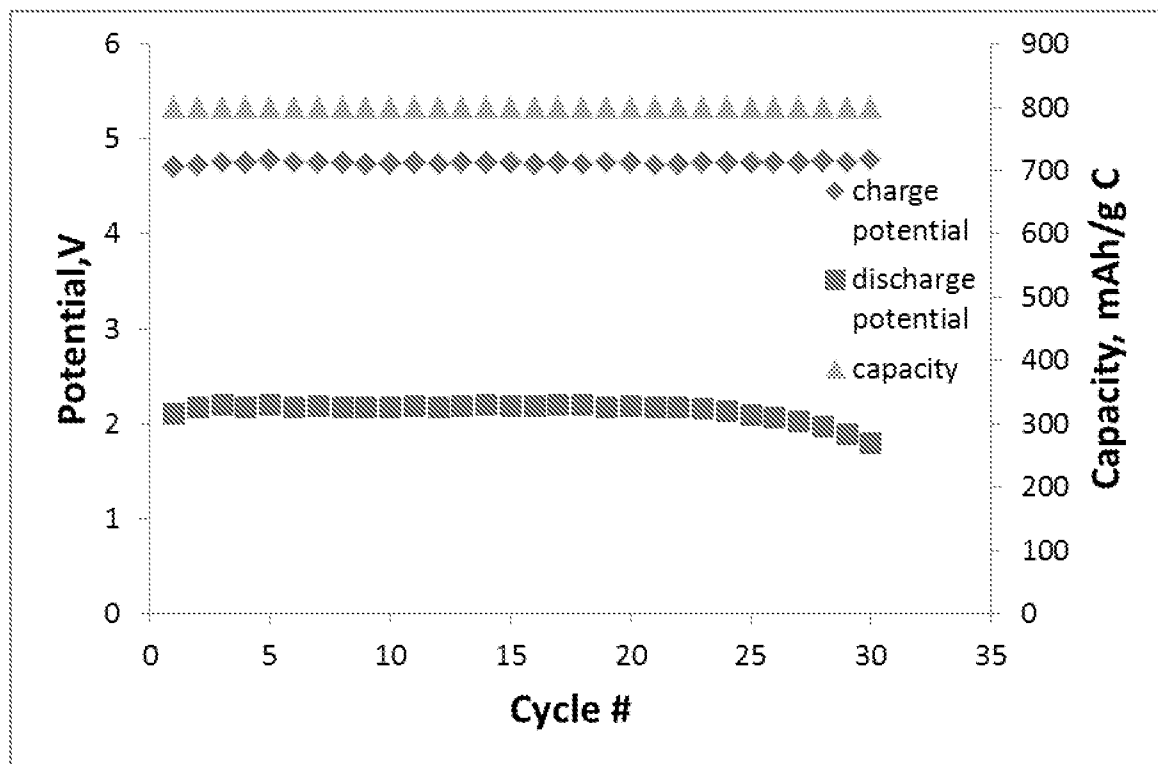
G. 12



G. 13

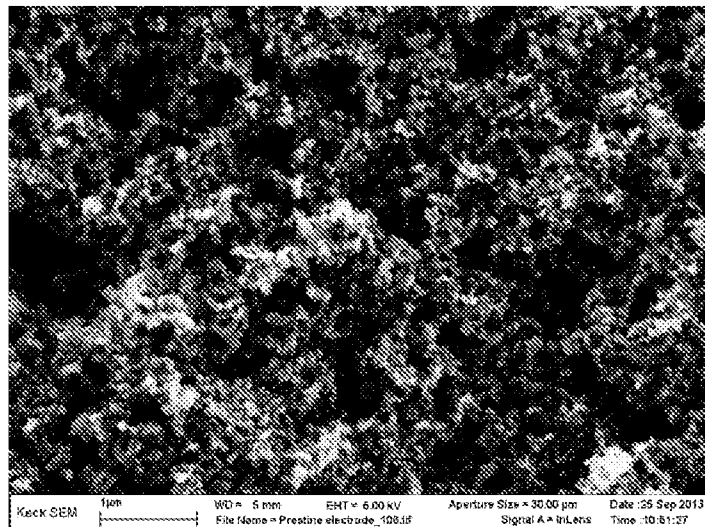


G. 14

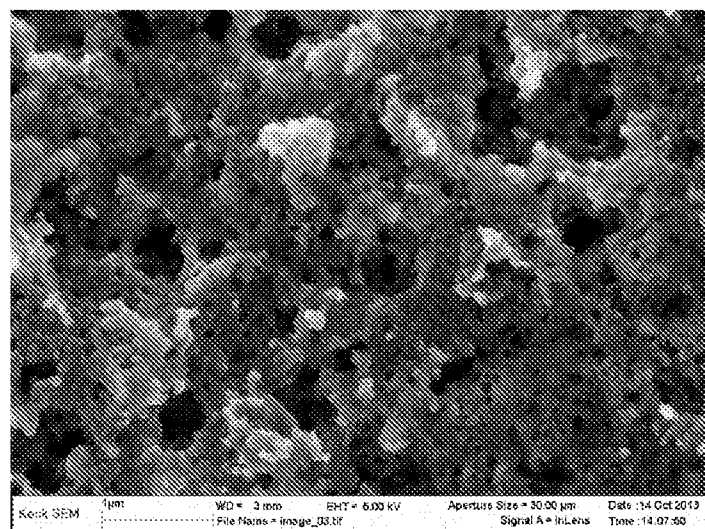


G. 15

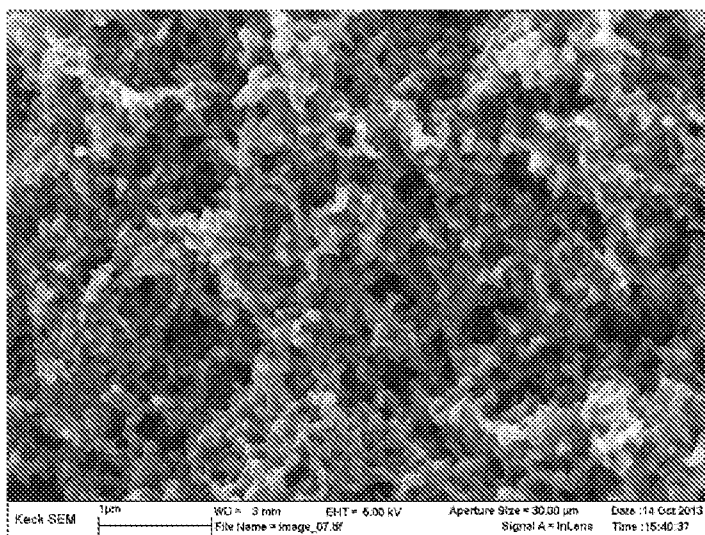
G. 16A

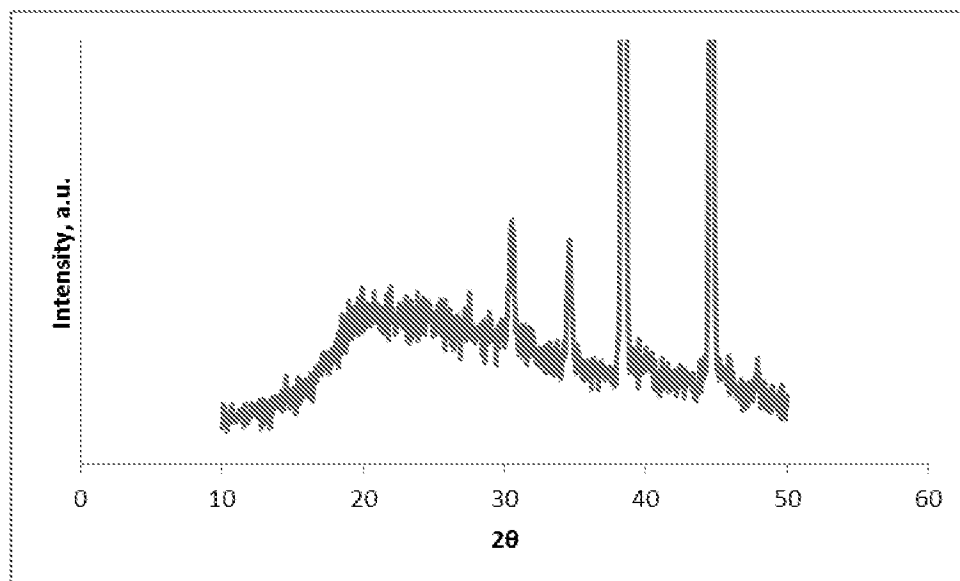


G. 16B

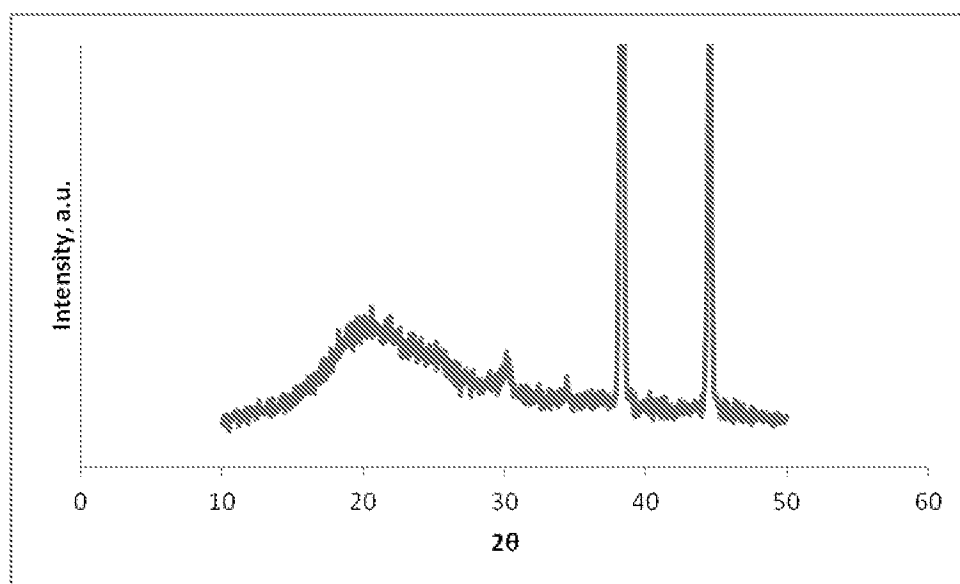


G. 16C





G. 17A



G. 17B

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/068469**A. CLASSIFICATION OF SUBJECT MATTER****H01M 12/06(2006.01)i, H01M 4/134(2010.01)i, H01M 10/36(2006.01)i**

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)

H01M 12/06; H01M 8/18; C25B 9/00; H01M 10/40; H01M 10/24; H01M 8/06; H01M 6/16; C25B 15/00; H01M 10/26; H01M 4/134; H01M 10/36

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: carbon dioxide, metal-oxygen battery, fuel, ratio, temperature

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012-0094193 A1 (PAUL ALBERTUS et al.) 19 April 2012 See paragraphs [0011]-[0033], claims 1-19 and figure 3.	1-22
A	US 2007-0065686 A1 (QINBAI FAN et al.) 22 March 2007 See paragraphs [0019]-[0025], claim 1 and figure 1.	1-22
A	US 5593552 A (ASHOK V. JOSHI et al.) 14 January 1997 See abstract, column 2, line 46 - column 5, line 34 and claim 1.	1-22
A	US 2004-0234865 A1 (TAKAYA SATO et al.) 25 November 2004 See abstract, paragraphs [0047]-[0087] and claims 1-3.	1-22
A	JP 2001-210364 A (MITSUBISHI CHEMICALS CORP.) 03 August 2001 See abstract, paragraph [0029] and claims 1-10.	1-22



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

19 February 2014 (19.02.2014)

Date of mailing of the international search report

20 February 2014 (20.02.2014)

Name and mailing address of the ISA/KR

Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City,
302-701, Republic of Korea

Facsimile No. +82-42-472-7140

Authorized officer

KIM, Seung Beom

Telephone No. +82-42-481-3371



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2013/068469

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