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(54) Title of the Invention: **Electrolyte, niobium battery including the electrolyte, and method of manufacture thereof**

Abstract Title: **Electrolyte, niobium battery including the electrolyte, and method of manufacture thereof**

(57) A secondary battery comprises a positive electrode; a negative electrode comprising a niobium metal oxide; a separator between the positive electrode and the negative electrode; and an electrolyte comprising a solvent composition comprising a dinitrile solvent and at least one of a mononitrile solvent, a carbonate solvent, an ester solvent, or an ether solvent, wherein the dinitrile is contained in an amount of at least 0.1 weight percent, based on a total weight of the solvent composition, and a lithium salt. The electrolyte mitigates gas generation from reaction between the electrolyte and the niobium metal oxide in the negative electrode, improving safety of the battery. The dinitrile may comprise glutaronitrile, adiponitrile, pimelonitrile, suberonitrile, azelanitrile, sebaconitrile or a combination thereof, most preferably adiponitrile. A method of manufacturing the battery is also disclosed.

FIG. 1

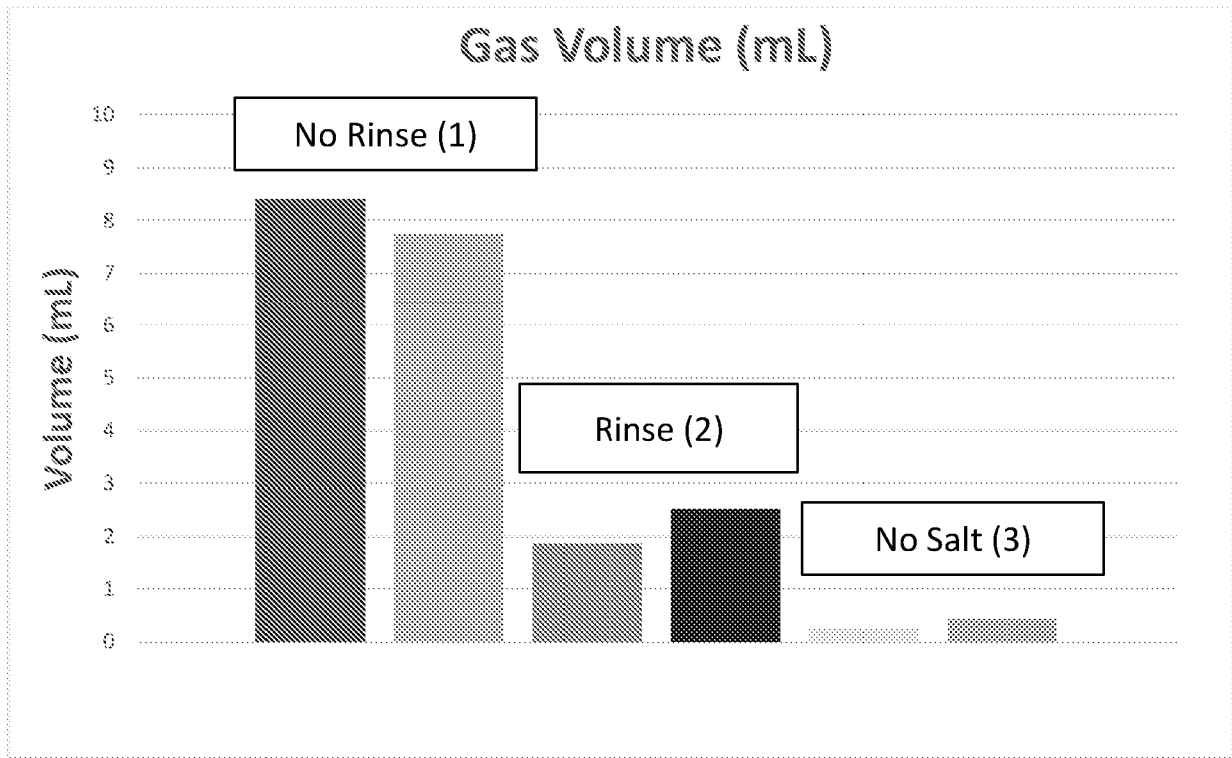


FIG. 2

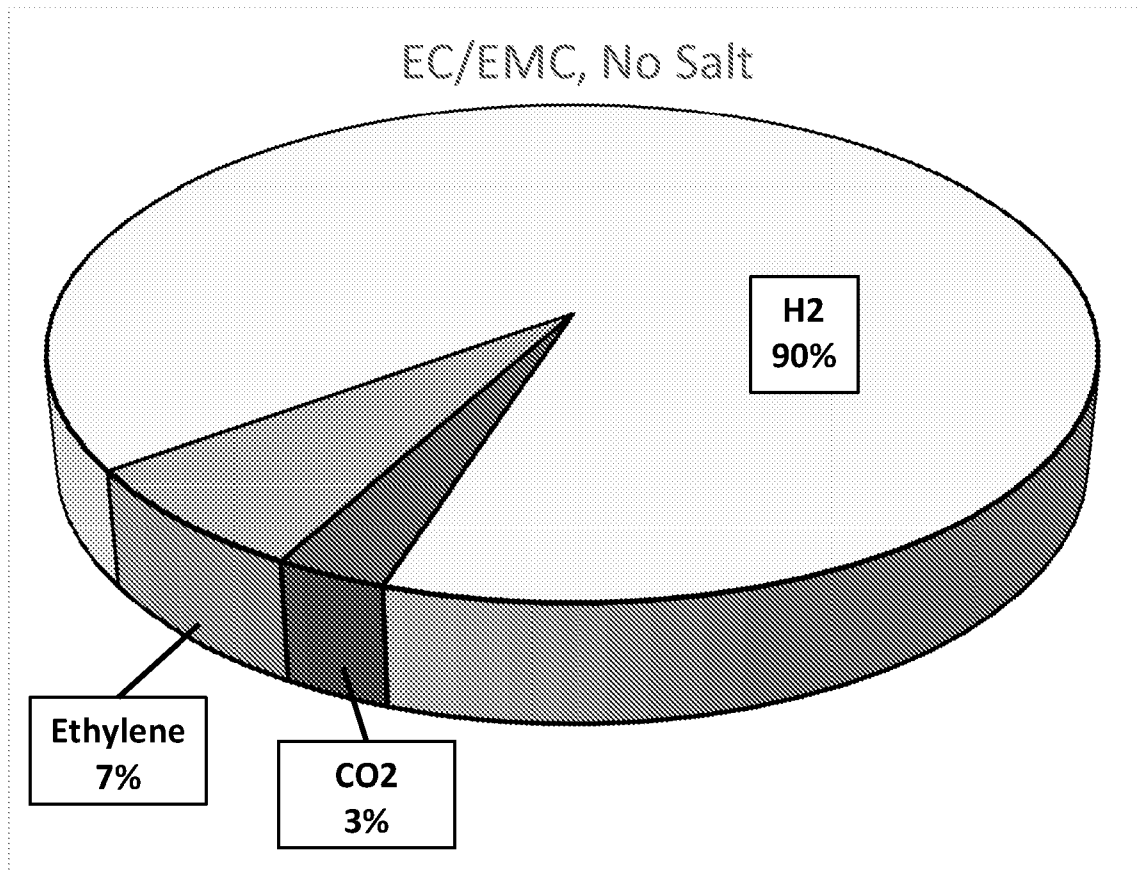


FIG. 3

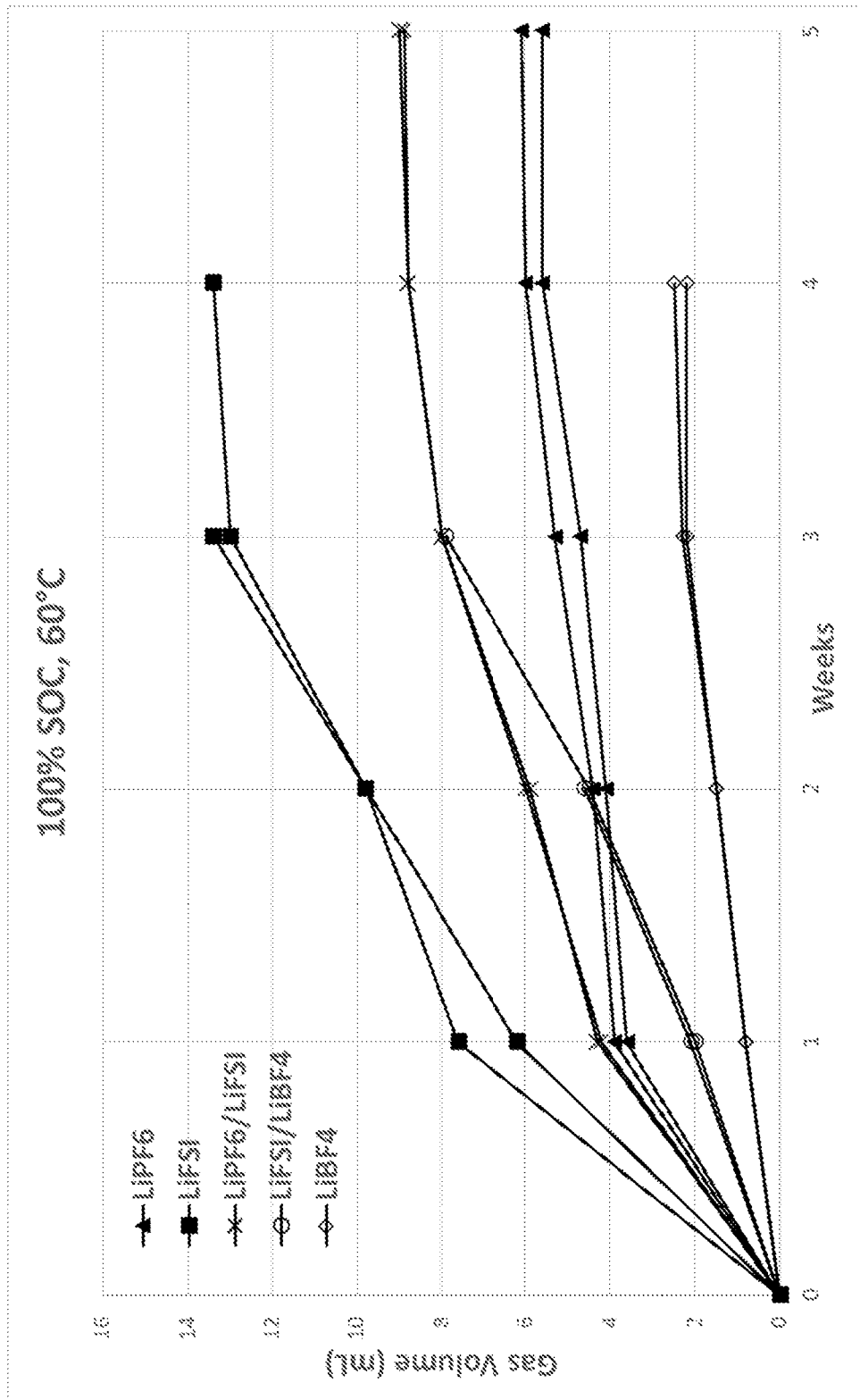


FIG. 4

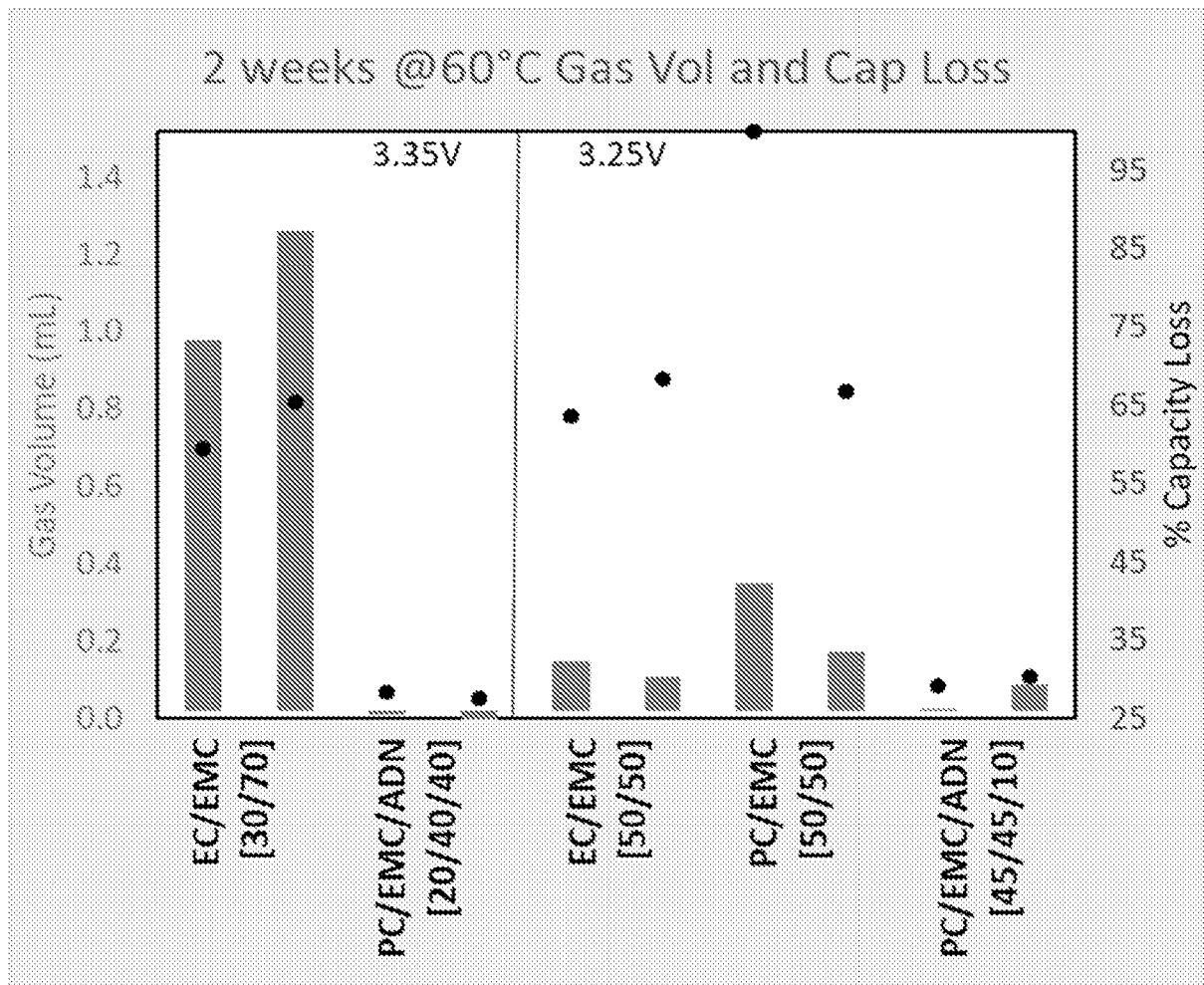
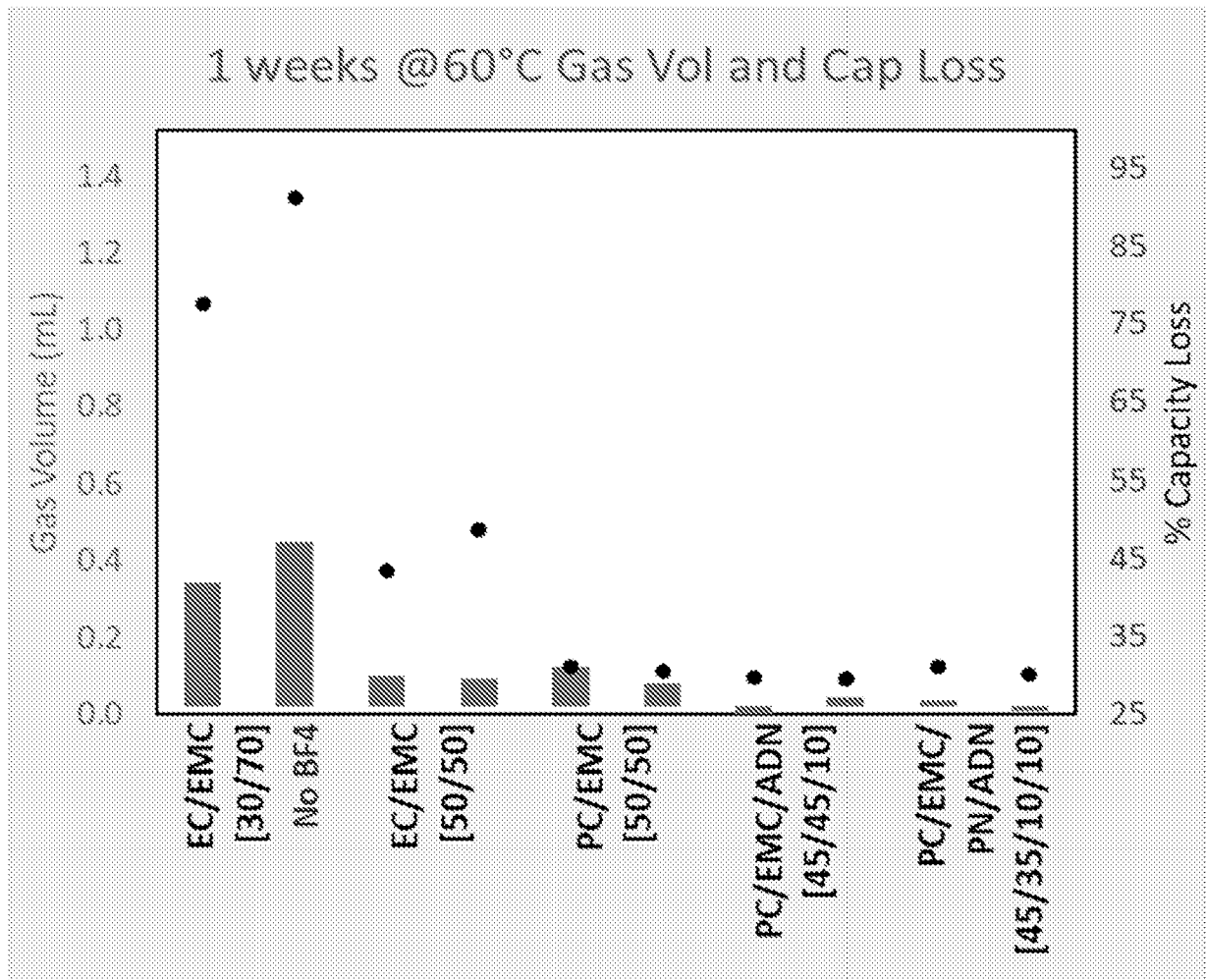


FIG. 5



ELECTROLYTE, NIOBIUM BATTERY INCLUDING THE ELECTROLYTE, AND METHOD OF MANUFACTURE THEREOF

BACKGROUND

[0001] During storage of a niobium battery undesirable gas generation can result.
5 There thus remains a need for improved materials for a niobium-based battery in which gas formation is reduced.

SUMMARY

[0002] Disclosed is a secondary battery, comprising: a positive electrode; a negative
10 electrode comprising a niobium metal oxide; a separator between the positive electrode and the negative electrode; and an electrolyte comprising a solvent composition comprising a dinitrile solvent and at least one of a carbonate solvent, an ester solvent, or an ether solvent, wherein the dinitrile is contained in an amount of at least 0.1 weight percent, based on a total weight of the solvent composition, and a lithium salt.

[0003] Also disclosed is a method of manufacturing a secondary battery, the method
15 comprising: providing a positive electrode, providing a negative electrode comprising a niobium metal oxide, and providing a separator between the positive electrode and the negative electrode; and providing an electrolyte comprising a solvent composition comprising a dinitrile solvent and at least one of a carbonate solvent, an ester solvent, or an ether solvent, wherein the dinitrile is contained in an amount of at least 0.1 weight percent, based
20 on a total weight of the solvent composition, and a lithium salt, and contacting the positive electrode, the negative electrode, and the separator with the electrolyte to manufacture the secondary battery.

[0004] The above described and other features are exemplified by the following figures and detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0005] The following figures are exemplary embodiments wherein the like elements are numbered alike.

[0006] FIG. 1 is a graph showing the volume of gas generated in lithium nickel cobalt aluminum oxide (NCA)/niobium tungsten oxide (NWO) pouch cells during storage of the cells
30 for 7 days at 60°C.

[0007] FIG. 2 is a pie chart illustrating the composition of gases generated in an NCA/NWO pouch cell containing an electrolyte without salt.

[0008] FIG. 3 is a graph showing the volume of gas generated over time (weeks) for NCA/NWO pouch cells containing electrolytes with different lithium salts.

[0009] FIG. 4 is a graph showing the volume of gas generated and the percentage capacity lost in LCO/NWO pouch cells containing different electrolytes following storage of the cells for 14 days at 60°C.

5 [0010] FIG. 5 is a graph showing the volume of gas generated and the percentage capacity lost in LCO/NWO pouch cells containing different electrolytes following storage of the cells for 7 days at 60°C.

DETAILED DESCRIPTION

[0011] Secondary batteries including a niobium oxide or niobium metal oxide negative electrode produce significant amounts of gas when the cells are in a charged state. It has
10 been discovered that gas generation is affected by the composition of the electrolyte. For example, when the electrolyte includes a cyclic carbonate (e.g., ethylene carbonate) reduction of the cyclic carbonate can occur in the presence of a niobium-based negative electrode. Interactions between the electrolyte and niobium-based negative electrode can result in the reduction of the electrolyte to generate hydrogen and oxygen, particularly when
15 the cells are held in a charged state or at elevated temperature. In cells including a niobium oxide or niobium metal oxide negative electrode, the decomposition of the electrolyte can be autocatalytic and involve reaction of the fluorinated salt with residual alcohol or water in the electrolyte solvent and reduction of cyclic carbonate (if present), resulting in gas generation. Generated hydrogen and oxygen accumulate within the battery and can become a hazard.

20 [0012] Cells where the negative electrode potential can be lowered to a voltage suitable to form a solid-electrolyte interphase (SEI) avoid this problem. For example, in cells with graphite-based negative electrode this gassing problem is not present because the solid-electrolyte interphase (SEI) is formed when the negative electrode potential vs. lithium is at a voltage of less than 0.2 volts (V) versus Li. The SEI is understood to passivate the negative
25 electrode surface, avoiding reduction of the electrolyte. However, the SEI is also decomposed or removed at greater potentials, and thus this strategy is not available for niobium-based electrodes because they operate at potentials of greater than 0.2V vs Li.

[0013] Also, use of sacrificial additives (e.g., vinylene carbonate, or 1,3-propane sultone) in the electrolyte to encourage the formation of a SEI is not satisfactory for niobium-
30 based negative electrodes because when the cells are charged and discharged, the cells are cycle-swept across a range of reduction-oxidation potentials that results in decomposition of the SEI. Furthermore, the SEI forms a resistive barrier that hinders charge and discharge rates, thereby negatively impacting one of the key attributes of a niobium-based negative electrode.

35 [0014] Disclosed herein are electrolytes that mitigate gas generation and improve safety of a lithium-ion secondary battery including a niobium oxide or niobium metal oxide negative electrode. In particular, it has been advantageously discovered that an electrolyte

comprising a dinitrile solvent in combination with one or more specific lithium salts and a carbonate, ester, and/or ether solvent, effectively decreases the amount of gas generated.

5 [0015] The electrolyte disclosed herein is non-aqueous and comprises a solvent composition and a lithium salt. The solvent composition comprises a dinitrile solvent and at least one of mononitrile solvent, a carbonate solvent, an ester solvent, or an ether solvent.

10 [0016] The dinitrile is a C₃ to C₁₀ aliphatic linear dinitrile. The aliphatic group of the C₂ to C₁₀ aliphatic linear dinitrile can be a substituted or unsubstituted linear C₃ to C₂₀ alkyl, alkenyl, or alkynyl group. Examples of the C₃ to C₁₀ aliphatic linear dinitrile include glutaronitrile (GN; pentanedinitrile), adiponitrile (ADN; hexanedinitrile), pimelonitrile (PMN; heptanedinitrile), suberonitrile (SUN; octanedinitrile), azelanitrile (AZN; nonanedinitrile), sebaconitrile (SEN; decanedinitrile), or a combination thereof.

15 [0017] The carbonate solvent comprises a C₃ to C₉ linear carbonate. Examples include dimethyl carbonate (DMC), diethyl carbonate (DEC), dipropyl carbonate (DPC), methyl propyl carbonate (MPC), methyl iso-propyl carbonate, ethyl propyl carbonate (EPC), ethyl iso-propyl carbonate, ethyl methyl carbonate (EMC), methyl ethyl carbonate (MEC), ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate (BC), isobutylene carbonate, monofluoroethylene carbonate (FEC), 4,4-difluoroethylene carbonate, 4,5-difluoroethylene carbonate, or a combination thereof.

20 [0018] The ether solvent comprises dibutyl ether, tetraglyme, diglyme, 1,2-dimethoxyethane, 2-methyl tetrahydrofuran, tetrahydrofuran, or a combination thereof.

[0019] The ester solvent comprises a C₃ to C₉ linear ester. Examples include methyl acetate, ethyl acetate, n-propyl acetate, isopropyl acetate, dimethyl acetate, methyl propionate, ethyl propionate, γ -butyrolactone, 5-decanolide, γ -valerolactone, dl-mevalonolactone, γ -caprolactone, or a combination thereof.

25 [0020] The dinitrile solvent is contained in the solvent composition in an amount of at least 0.1 weight percent (wt%), or at least 0.5 wt%, or at least 1 wt%, or at least 5 wt%, or at least 10 wt%. In an aspect, the dinitrile solvent is contained in the solvent composition in an amount 0.1 wt% to 55 wt%, or 0.2 wt% to 50 wt%, or 1 wt% to 45 wt%, or 5 wt% to 40 wt%, or 5 wt% to 30 wt%, or 10 wt% to 30 wt%, or 10 wt% to 25 wt%, or 10 wt% to 20 wt%, based on the total weight of the solvent composition.

35 [0021] In an aspect, the total amount of mononitrile solvent, carbonate solvent, ester solvent, and/or ether solvent contained in the solvent composition is 1 wt% to 99.8 wt%, or 20 wt% to 99.8 wt%, or 30 wt% to 99 wt%, or 40 wt% to 95 wt%, or 50 wt% to 95 wt%, or 70 wt% to 90 wt%, or 75 wt% to 90 wt%, or 80 wt% to 90 wt%, based on the total weight of the solvent composition.

[0022] In an aspect, the weight ratio of the dinitrile solvent to the total amount of mononitrile solvent, carbonate solvent, ester solvent, and/or ether solvent can be 5:1 to 1:20, or 3:1 to 1:20, or 2:1 to 1:10, or 1:1 to 1:10, or 1:2 to 1:10, or 1:3 to 1:10.

5 [0023] In an aspect, the solvent composition comprises the carbonate solvent. In an aspect, the carbonate solvent comprises PC, EMC, or a combination thereof. In an aspect, the carbonate solvent consists of PC, EMC, or a combination thereof. In an aspect, the carbonate comprises EC or PC, and the EC or PC is contained in an amount of at least 1 weight percent, based on a total weight of the solvent composition. In an aspect, the EC or PC is contained in an amount of at least 1 wt%, at least 5 wt%, at least 10 wt%, or at least 20
10 wt% based on the total weight of the solvent composition. In an aspect the EC or PC is contained in an amount of 1 wt% to 60 wt%, or 5 wt% to 45 wt%, or 10 wt% to 40 wt%, based on the total weight of the solvent composition.

[0024] In an aspect, the solvent composition includes the mononitrile solvent. In an aspect, the mononitrile solvent comprises a C₂ to C₈ aliphatic mononitrile. The aliphatic group
15 of the C₂ to C₈ aliphatic mononitrile can be a linear or branched C₂ to C₈ alkyl, alkenyl, or alkynyl group, and in an aspect, is a linear C₂ to C₈ alkyl, alkenyl, or alkynyl group. Examples of the mononitrile include methoxypropionitrile, butyronitrile, ethanenitrile, propanenitrile (propionitrile), acetonitrile, or a combination thereof. In an aspect, the mononitrile solvent is contained in the solvent composition in an amount of 1 wt% to 95wt%, or 5 wt% to 90 wt%, or
20 10 wt% to 85 wt %, or 10 wt% to 75 wt%, or 20 wt% to 50 wt%, based on the total weight of the solvent composition. In an aspect, the mononitrile solvent is contained in the solvent composition in an amount of 5% to 50 wt%, or 10 wt% to 40 wt%.

[0025] In an aspect, the solvent composition comprises the dinitrile solvent and the mononitrile solvent, and the total amount of carbonate solvent, ether solvent, and ester
25 solvent in the solvent composition is from 0.01 wt% to 10 wt%, or from 0.05 wt% to 5 wt%, or 0.1 wt% to 1 wt%, based on the total weight of the solvent composition. In an aspect, the solvent composition comprises the dinitrile solvent and the mononitrile solvent and substantially no carbonate solvent, ester solvent, or ether solvent.

[0026] In an aspect, the solvent consists of PC or EC, EMC, and ADN. In an aspect,
30 the solvent composition comprises, or consists of 30 wt% PC or EC, 60 wt% EMC, and 10 wt% ADN.

[0027] The lithium salt in the electrolyte comprises LiBF₄, LiPF₆, lithium bis(fluorosulfonyl)imide (LiFSI), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), or a combination thereof. The concentration of the lithium salt in the nonaqueous electrolyte is, for
35 example, 0.01 molar (M) to 2.0 M, 0.05 M to 1.8 M, 0.1 M to 1.6 M, 0.5 M to 1.4 M, 0.5 M to 1.3 M, or 0.8 M to 1 M' based on the total weight of the electrolyte. In an aspect, the lithium salt comprises 0.01 to 1 M LiBF₄ and 0.1 M to 0.3 M of LiPF₆.

[0028] In an aspect, the electrolyte comprises 0.5 M to 3 M lithium salt and is substantially free of PF_6^- . In an aspect, the electrolyte comprises less than 0.1 M, or less than 0.05 M, or less than 0.02 M, or less than 0.01 M, or less than 0.005 M of PF_6^- . In an aspect, the electrolyte does not comprise PF_6^- .

5 [0029] The solvent composition can be prepared by combining the dinitrile solvent and at least one of the carbonate solvent, the ester solvent, or the ether solvent. The electrolyte can be prepared by contacting the solvent composition with the lithium salt and dissolving the lithium salt in the solvent composition.

10 [0030] Also disclosed is a secondary battery comprising the electrolyte described herein. In particular, the secondary battery comprises: a positive electrode; a negative electrode comprising a niobium metal oxide; a separator between the positive electrode and the negative electrode; and the electrolyte.

[0031] The negative electrode comprises a negative electrode active material on the current collector. The negative electrode active material comprises a niobium metal oxide. 15 The niobium metal oxide has the formula $\text{Nb}_x\text{M}_y\text{O}_z$, where x is 2 to 34, y is 1 to 20, and z is 8 to 115, and M is Na, Mg, Al, Si, P, S, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Y, Zr, Mo, In, Sn, Sb, Ta, W, or a combination thereof. In an aspect, M is V, Cr, Mo, Ta, W, P, S, or a combination thereof. In an aspect, the niobium metal oxide comprises niobium, tungsten or molybdenum, and optionally calcium, chromium, cobalt, magnesium, manganese, nickel, 20 potassium, phosphorus, sodium, sulfur, or a combination thereof. In an aspect, the niobium metal oxide is a niobium tungsten oxide or a niobium molybdenum oxide. In an aspect, the niobium metal oxide comprises niobium, tungsten or molybdenum, and oxygen. Examples of the niobium tungsten oxide include $\text{Nb}_{14}\text{W}_3\text{O}_{44}$, $\text{Nb}_{16}\text{W}_5\text{O}_{55}$, $\text{Nb}_{18}\text{W}_8\text{O}_{69}$, Nb_2WO_8 , $\text{Nb}_{18}\text{W}_{16}\text{O}_{93}$, $\text{Nb}_{22}\text{W}_{20}\text{O}_{115}$, $\text{Nb}_2\text{Mo}_3\text{O}_{14}$, $\text{Nb}_{14}\text{Mo}_3\text{O}_{44}$, $\text{Nb}_{12}\text{MoO}_{44}$, or a combination thereof. In an aspect, the 25 niobium metal oxide comprises $\text{Nb}_{16}\text{W}_5\text{O}_{55}$. Use of niobium oxide (e.g., Nb_2O_5 , NbO_2 , $\text{Nb}_{12}\text{O}_{29}$, or $\text{Nb}_{25}\text{O}_{62}$) is also mentioned. Also mentioned is an aspect where the niobium oxide is doped to provide a compound of the formula $\text{Nb}_x\text{M}1_{y1}\text{M}2_{y2}\text{O}_z$, where M1 is W or Mo, M2 is V, Cr, Mo, Ta, W, P, S, or a combination thereof, x is 2 to 34, $(y1+y2)$ is 1 to 20, and z is 8 to 115, $0 \leq y1 \leq 20$ and $0 \leq y2 \leq 20$.

30 [0032] The negative electrode active material may further include an additional active material. Examples of the additional negative electrode active material include tungsten oxide, lithium titanium oxide, or a combination thereof.

[0033] The negative electrode can be formed from a negative electrode composition comprising the negative electrode active material. In addition to the negative electrode active 35 material, the negative electrode composition can further comprise a binder, a solvent, a conductive agent, or a combination thereof. The binder can include polyvinylalcohol, carboxymethylcellulose, hydroxypropylcellulose, diacetylcellulose, polyvinylchloride, carboxylated polyvinylchloride, polyvinylfluoride, ethylene oxide-containing polymer, polyvinylpyrrolidone, polyurethane, polytetrafluoroethylene, polyvinylidene fluoride,

polyethylene, polypropylene, styrene-butadiene rubber, acrylated styrene-butadiene rubber, an epoxy resin, nylon, or a combination thereof. The conductive agent can include a conductive carbon such as carbon nanotubes, natural graphite, artificial graphite, carbon black, acetylene black, ketjen black, and carbon fiber, or a powder or fiber of a metal such as copper, nickel, aluminum, or silver.

[0034] In an aspect, the negative electrode comprises a negative electrode composition disposed on an aluminum current collector, the negative electrode composition comprising, or consisting of, $Nb_{16}W_5O_{55}$ as the negative active material, SBR as the binder, and conductive carbon, as the conductive agent.

[0035] Alternatively, the negative electrode current collector can include copper, nickel, stainless steel, carbon steel, titanium, or a combination thereof.

[0036] The negative electrode may be formed by coating a layer of the negative electrode composition on a negative electrode current collector, or alternatively, the negative electrode composition may be cast onto a separate support and a film exfoliated from the separate support laminated on the metal current collector. The method of preparing the negative electrode is not limited thereto, and any other method suitable for the preparation of a negative electrode may also be used.

[0037] The positive electrode comprises a positive electrode active material. The positive electrode can comprise lithium cobalt oxide (LCO), lithium nickel cobalt aluminum oxide (NCA), lithium manganese oxide (LMO), lithium nickel manganese oxide (LNMO), lithium nickel cobalt manganese oxide (NMC), lithium iron phosphate (LFP), lithium manganese iron phosphate (LMFP), or a combination thereof.

[0038] The positive electrode can be formed from a positive electrode composition comprising the positive electrode active material. In addition to the positive electrode active material, the positive electrode composition can further comprise a binder, a solvent, a conductive agent, or a combination thereof. The conductive agent can include carbon nanotubes, natural graphite, artificial graphite, carbon black, acetylene black, ketjen black, carbon fiber, a powder or fiber of a metal such as copper, nickel, aluminum, or silver, or a combination thereof. The binder in the positive electrode composition can include polyvinylalcohol (PVA), carboxymethylcellulose (CMC), hydroxypropyl cellulose, diacetyl cellulose, polyvinylchloride, carboxylated polyvinylchloride, polyvinyl fluoride, polyethylene oxide, polyvinylpyrrolidone, polyurethane, polytetrafluoroethylene, polyvinylidene fluoride, polyethylene, polypropylene, styrene-butadiene rubber, acrylated styrene-butadiene rubber, epoxy resin, nylon, or a combination thereof. In an aspect, the positive electrode comprises a positive electrode composition on an aluminum current collector, the positive electrode composition comprising, or consisting of, NMC or LCO as the positive electrode active material, PVDF as a binder, and carbon nanotubes, carbon black, and/or ketjen black as a conductive agent.

[0039] The positive electrode can further include a positive current collector comprising aluminum, titanium, stainless steel, carbon, or a combination thereof.

[0040] The positive electrode can be prepared in a manner similar to the method described above for the negative electrode.

5 [0041] The secondary battery comprises a separator between the positive and the negative electrodes. The separator is not limited and can be any separator suitable for use in a lithium-ion battery. The separator comprises a separator material that is electrically insulating, chemically non-reactive with the positive and negative active materials, chemically non-reactive with the electrolyte, and insoluble in the electrolyte. In addition, the separator
10 material is selected such that it has a degree of porosity sufficient to allow the electrolyte to flow through during the electrochemical reaction of the cell. The separator can be a porous polymer membrane, or can be a non-woven or woven fabric. The separator can comprise, for example, polypropylene (e.g., Celgard® 2500), polyethylene, polyamide (nylon), polysulfone, polyvinyl chloride (PVC), polyvinylidene fluoride (PVDF), polyvinylidene fluoride-co-
15 hydrofluoropropylene (PVDF-HFP), a tetrafluoroethylene-ethylene copolymer (PETFE), a chlorotrifluoroethylene-ethylene copolymer, or a combination thereof. In an aspect, the separator can comprise two or more layers of alternating materials, for example, a trilayer separator of polypropylene / polyethylene / polypropylene. The separator can be impregnated with the electrolyte.

20 [0042] The cell is manufactured by providing the nonaqueous electrolyte and adding the nonaqueous electrolyte to an assembly comprising the positive electrode, the negative electrode, and the separator between the positive and negative electrodes.

[0043] The secondary battery can be of any configuration, such as a cylindrical wound cell, a prismatic cell, a rigid laminar cell, or a flexible pouch, envelope or bag cell.

25 [0044] The secondary battery including a niobium metal oxide as negative active material and the electrolytes disclosed herein demonstrates reduced gas production. In particular, relatively low amounts of gas are produced by the secondary battery during extended storage at a temperature of 50°C to 70°C, or 55°C to 65°C, or 60°C. The disclosed secondary battery has a gas generation volume of less than 10 vol%, or less than 8 vol%, or
30 less than 5 vol%, or less than 3 vol%, or less than 1 vol%, or less than 0.1 vol%, following storage of the secondary battery for 6 days at 60°C, based on a total volume of the cell. The disclosed secondary battery also has a gas generation volume of 0.001 vol%, 0.01 vol%, or 0.1 vol% to 1 vol%, 5 vol%, or 10 vol%, based on a total volume of the cell following storage for 14 days at 60°C. In an aspect, the gas volume is less than 10% of the total cell volume
35 following storage for 3 months at 60°C.

[0045] This disclosure is further illustrated by the following examples, which are non-limiting.

EXAMPLES

Example 1

[0046] A multi-layer pouch cell including lithium nickel cobalt aluminum oxide (LiNi_xCo_yAl_zO₂, where $x \geq 0.8$, $z \leq 0.05$ and $x + y + z = 1$, NCA) as the positive electrode active material and the niobium tungsten oxide Nb₁₆W₅O₅₅ (NWO) as the negative electrode active material, was filled with an electrolyte containing 1 M LiPF₆ and the solvents ethylene carbonate (EC) and ethyl methyl carbonate (EMC) in a EC:EMC weight ratio of 30:70, and charged to 3 V. The electrode stack was extracted from the charged full cell and separated into individual negative electrode layers each with a capacity of ~80 mAh. In this state, the NWO negative electrode is fully lithiated and at a potential of ~1.1 V vs. lithium.

[0047] A first negative electrode layer (1) was not-rinsed and not placed in a pouch with fresh electrolyte, a second negative electrode layer (2) was rinsed and placed in a pouch with fresh electrolyte, and a third negative electrode layer (3) was rinsed and placed in a pouch with only 30:70 EC:EMC solvent, i.e., without LiPF₆ salt.

[0048] Figure 1 shows the gas volume generated through interaction between the NWO negative electrode and the other material contained in the pouch, i.e., in the cases of layers (1) and (2) the electrolyte and in the case of layer (3) the solvent. Layer (1), which was not rinsed and therefore had a higher salt concentration, generated the highest volume of gas. Layer (2), which was rinsed and then contacted with the 30:70 EC:EMC electrolyte, produced a lower volume of gas, but the volume was still greater than that produced by layer (3). Accordingly, decreased salt concentration ($1 > 2 > 3$) led to decreased gas volume as the autocatalytic decomposition of LiPF₆ was less pronounced.

Example 2

[0049] The composition of the gas produced by the no-salt pouch (third negative electrode layer) in Example 1, was measured by gas chromatography to determine the role of the solvent in gas generation, independent of the salt. The results are shown in FIG. 2, where it can be seen that a significant percentage of the gas was composed of ethylene (the gas was made up of 90% hydrogen, 3% carbon dioxide, 7% ethylene), indicating reduction of the electrolyte solvent EC. It was concluded from these experiments that a benefit could be gained by using a salt and solvent package tailored to reduce interaction with the NWO negative electrode.

Example 3

[0050] The effect of lithium salt on gas generation was evaluated. Multi-layer 0.6 ampere-hour (Ah) NCA/NWO pouch cells were prepared and filled with one of the following electrolytes: 1 M LiPF₆ and 30:70 EC:EMC, 1 M LiFSI and 30:70 EC:EMC, or 1 M LiBF₄ and

30:70 EC:EMC. The cell was charged to 3V such that the NWO negative electrode is fully lithiated and at a potential of ~1.1 V vs. lithium. The cell was stored in a 60 °C oven and the gas volume was periodically measured as described in Example 1.

5 [0051] The results (FIG. 3) indicate that use of a LiBF₄ salt significantly reduces gassing compared to LiPF₆ or LiFSI.

Example 4

10 [0052] The effect of electrolyte solvent on gas generation was evaluated. Multi-layer 0.16 Ah LCO/NWO pouch cells were filled with electrolyte containing 1.1 M of 20% LiBF₄/80% LiPF₆ salt in different solvents, formed, and charged to 3.35V or 3.25V. A mixture of
15 LiBF₄/LiPF₆, rather than pure LiBF₄, was used to provide improved conductivity of the electrolyte while avoiding gassing. The solvents adiponitrile (ADN), propionitrile (PN), and propylene carbonate (PC) were tested, based on their stability against reduction at low voltages vs. Li. The electrolyte compositions tested are shown Table 1 below. Once assembled, the pouches were stored for 14 days at 60°C and the gas volume was measured
as described in Example 1. The capacity of the cell was also measured by discharging at C/2 to 1.3 V and compared to the initial capacity.

Table 1

Salt(s) Salt Amounts (%)	Solvents	Solvent Weight Ratio
LiBF ₄ : LiPF ₆ 20:80	EC:EMC	30:70
LiBF ₄ : LiPF ₆ 20:80	PC:EMC:ADN	20:40:40
LiBF ₄ : LiPF ₆ 20:80	EC:EMC	50:50
LiBF ₄ : LiPF ₆ 20:80	PC/EMC	50:50
LiBF ₄ : LiPF ₆ 20:80	PC:EMC:ADN	45:45:10
LiBF ₄ : LiPF ₆ 20:80	PC:EMC:PN:ADN	45:35:10:10
LiPF ₆ 100%	EC:EMC	30:70

[0053] As shown in FIG. 4, cells that are charged to 3.35 V show significantly less gassing and lower capacity loss when the solvent is 20:40:40 PC:EMC:ADN, indicating stability of this solvent system. Cells including a blend of 45:45:10 PC:EMC:ADN, when charged to 3.25 V, have less gassing and lower capacity loss than cells including a blend of 30:70 EC:EMC. These cells also have less gassing and capacity loss than a 50:50 blend of PC:EMC, indicating that ADN is a critical component for solvent stability.

[0054] 10% of EMC in the 45:45:10 PC:EMC:ADN was replaced with PN in order to reduce viscosity. The cells were stored for 7 days at 60°C, resulting in minimal gassing and capacity loss. The results in FIG. 5 show that PN improves electrochemical performance of cells containing PC and ADN.

[0055] As demonstrated in the examples, use of selected salt and solvent combinations provide reduced gassing for niobium oxide or niobium metal oxide negative electrode.

[0056] The compositions, methods, and articles can alternatively comprise, consist of, or consist essentially of, any appropriate materials, steps, or components herein disclosed.

The compositions, methods, and articles can additionally, or alternatively, be formulated so as to be devoid, or substantially free, of any materials (or species), steps, or components, that are otherwise not necessary to the achievement of the function or objectives of the compositions, methods, and articles.

5 [0057] It will be understood that when an element is referred to as being "on" another element, it can be directly on the other element or intervening elements may be present therebetween. In contrast, when an element is referred to as being "directly on" another element, there are no intervening elements present.

10 [0058] All ranges disclosed herein are inclusive of the endpoints, and the endpoints are independently combinable with each other (e.g., ranges of "up to 25 wt.%, or, more specifically, 5 wt.% to 20 wt.%" is inclusive of the endpoints and all intermediate values of the ranges of "5 wt.% to 25 wt.%" etc.). "Combinations" is inclusive of blends, mixtures, alloys, reaction products, and the like. The terms "first," "second," and the like, do not denote any order, quantity, or importance, but rather are used to distinguish one element from another.

15 The terms "a" and "an" and "the" do not denote a limitation of quantity and are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. "Or" means "and/or" unless clearly stated otherwise. Reference throughout the specification to "some embodiments", "an embodiment", and so forth, means that a particular element described in connection with the embodiment is included in at least

20 one embodiment described herein, and may or may not be present in other embodiments. In addition, it is to be understood that the described elements may be combined in any suitable manner in the various embodiments. A "combination thereof" is open and includes any combination comprising at least one of the listed components or properties optionally together with a like or equivalent component or property not listed

25 [0059] Unless defined otherwise, technical and scientific terms used herein have the same meaning as is commonly understood by one of skill in the art to which this application belongs. All cited patents, patent applications, and other references are incorporated herein by reference in their entirety. However, if a term in the present application contradicts or conflicts with a term in the incorporated reference, the term from the present application takes

30 precedence over the conflicting term from the incorporated reference.

[0060] Compounds are described using standard nomenclature. For example, any position not substituted by any indicated group is understood to have its valency filled by a bond as indicated, or a hydrogen atom. A dash ("-") that is not between two letters or symbols is used to indicate a point of attachment for a substituent. For example, -CHO is

35 attached through carbon of the carbonyl group.

[0061] "Aliphatic" or "aliphatic group" means a saturated or unsaturated linear or branched hydrocarbon group. An aliphatic group may be an alkyl, alkenyl, or alkynyl group, for example

[0062] "Nitrile" or "mononitrile" means a compound having the formula R-CN, where R is a substituted or unsubstituted C₂-C₂₀ aliphatic group. "Dinitrile" means a compound having the formula CN-R-CN, where R is a substituted or unsubstituted C₂-C₂₀ aliphatic group.

5 [0063] "Cyclic carbonate" refers to a carbonate compound having at least one ring and in which a carbonate group (-O(C=O)O-) forms a part of the ring. "Acyclic carbonate" refers to a carbonate compound wherein a carbonate group (-O(C=O)O-) does not form a part of the ring. The acyclic carbonate may include a linear hydrocarbon chain, a branched hydrocarbon chain, or both.

10 [0064] The term "alkyl" means a branched or straight chain, unsaturated aliphatic hydrocarbon group, e.g., methyl, ethyl, n-propyl, i-propyl, n-butyl, s-butyl, t-butyl, n-pentyl, s-pentyl, and n- and s-hexyl.

[0065] "Alkenyl" means a straight or branched chain, monovalent hydrocarbon group having at least one carbon-carbon double bond (e.g., ethenyl (-HC=CH₂)).

15 [0066] "Alkylene" means a straight or branched chain, saturated, divalent aliphatic hydrocarbon group (e.g., methylene (-CH₂-) or propylene (-CH₂)₃-).

[0067] "Substituted" means a compound or group substituted with at least one (e.g., 1, 2, 3, 4, 5, 6 or more) substituents independently selected from a halogen (e.g., F-, Cl-, Br-, I-), a hydroxyl, an alkoxy, a nitro, a cyano, an amino, an azido, an amidino, a hydrazino, a hydrazono, a carbonyl, a carbamyl, a thiol, a C₁ to C₆ alkoxy carbonyl, an ester, a carboxyl, or
20 a salt thereof, sulfonic acid or a salt thereof, phosphoric acid or a salt thereof, a C₁ to C₂₀ alkyl, a C₂ to C₁₆ alkynyl, a C₆ to C₂₀ aryl, a C₇ to C₁₃ arylalkyl, a C₁ to C₄ oxyalkyl, a C₁ to C₂₀ heteroalkyl, a C₃ to C₂₀ heteroaryl (i.e., a group that comprises at least one aromatic ring, wherein at least one ring member is other than carbon), a C₃ to C₂₀ heteroarylalkyl, a
25 C₃ to C₂₀ cycloalkyl, a C₃ to C₁₅ cycloalkenyl, a C₆ to C₁₅ cycloalkynyl, a C₅ to C₁₅ heterocycloalkyl, or a combination including at least one of the foregoing, instead of hydrogen, provided that the substituted atom's normal valence is not exceeded.

[0068] While particular embodiments have been described, alternatives, modifications, variations, improvements, and substantial equivalents that are or may be presently unforeseen may arise to applicants or others skilled in the art. Accordingly, the
30 appended claims as filed and as they may be amended are intended to embrace all such alternatives, modifications variations, improvements, and substantial equivalents.

Claims:

1. A secondary battery, comprising:

a positive electrode;

a negative electrode comprising a niobium metal oxide;

a separator between the positive electrode and the negative electrode; and

an electrolyte comprising

a solvent composition comprising a dinitrile solvent and at least one of a mononitrile solvent, a carbonate solvent, an ester solvent, or an ether solvent, wherein the dinitrile is contained in an amount of at least 0.1 weight percent, based on a total weight of the solvent composition, and

a lithium salt.
2. The secondary battery of claim 1, wherein the dinitrile is a C₃ to C₁₀ aliphatic linear dinitrile.
3. The secondary battery of claim 2, wherein the C₃ to C₁₀ aliphatic linear dinitrile comprises glutaronitrile, adiponitrile, pimelonitrile, suberonitrile, azelanitrile, sebaconitrile, or a combination thereof.
4. The secondary battery of claim 2, wherein the C₃ to C₁₀ aliphatic linear dinitrile is adiponitrile.
5. The secondary battery of any of claims 1 to 4, wherein the dinitrile is contained in an amount of 0.2 weight percent to 50 weight percent, based on a total weight of the solvent composition.
6. The secondary battery of any of claims 1 to 5, wherein the carbonate solvent comprises dimethyl carbonate, diethyl carbonate, dipropyl carbonate, methyl propyl carbonate, ethyl propyl carbonate, ethyl methyl carbonate, methyl ethyl carbonate, ethylene carbonate, propylene carbonate, butylene carbonate, monofluoroethylene carbonate, 4,4-difluoroethylene carbonate, 4,5-difluoroethylene carbonate, or a combination thereof.
7. The secondary battery of claim 6, wherein the carbonate solvent comprises propylene carbonate, and the propylene carbonate is contained in an amount of at least 1 weight percent, based on a total weight of the solvent composition

8. The secondary battery of any of claims 1 to 7, wherein the ester solvent comprises methyl acetate, ethyl acetate, n-propyl acetate, dimethyl acetate, methyl propionate, ethyl propionate, γ -butyrolactone, 5-decanolide, γ -valerolactone, dl-mevalonolactone, γ -caprolactone, or a combination thereof.

9. The secondary battery of any of claims 1 to 8, wherein the ether solvent comprises dibutyl ether, tetraglyme, diglyme, 1,2-dimethoxyethane, 2-methyl tetrahydrofuran, tetrahydrofuran, or a combination thereof.

10. The secondary battery of any of claims 1 to 9, wherein the mononitrile solvent comprises a C_2 to C_8 aliphatic mononitrile.

11. The secondary battery of claim 9, wherein the C_2 to C_8 aliphatic mononitrile comprises butyronitrile, ethanenitrile, proprionitrile, acetonitrile, or a combination thereof.

12. The secondary battery of claim 10, wherein the C_2 to C_8 aliphatic mononitrile is contained in an amount of 30 to 90 weight percent, based on a total weight of the solvent composition,

13. The secondary battery of any of claims 1 to 12, wherein the lithium salt comprises $LiBF_4$.

14. The secondary battery of any of claims 1 to 13, wherein the lithium salt is contained in the electrolyte in a concentration of 0.5 to 3 molar.

15. The secondary battery of claim 14, wherein the electrolyte comprises 0.01 to 0.3 molar $LiBF_4$.

16. The secondary battery of claim 14, wherein the electrolyte comprises 0.8 molar to 3 molar $LiPF_6$.

17. The secondary battery of claim 14, wherein the electrolyte comprises less than 0.1 molar PF_6^- .

18. The secondary battery of claim 14, wherein the electrolyte does not comprise PF_6^- .

19. The secondary battery of any of claims 1 to 18, wherein the niobium metal oxide is $Nb_{14}W_3O_{44}$, $Nb_{16}W_5O_{55}$, $Nb_{18}W_8O_{69}$, Nb_2WO_8 , $Nb_{18}W_{16}O_{93}$, $Nb_{22}W_{20}O_{115}$, $Nb_2Mo_3O_{14}$, $Nb_{14}Mo_3O_{44}$, $Nb_{12}MoO_{44}$, or a combination thereof.

20. The secondary battery of claim 19, wherein the niobium metal oxide is $Nb_{16}W_5O_{55}$.

21. A method of manufacturing a secondary battery, the method comprising:
providing a positive electrode,
providing a negative electrode comprising a niobium metal oxide, and
providing a separator between the positive electrode and the negative electrode; and
providing an electrolyte comprising

a solvent composition comprising a dinitrile solvent and at least one of a carbonate solvent, an ester solvent, or an ether solvent, wherein the dinitrile is contained in an amount of at least 0.1 weight percent, based on a total weight of the solvent composition, and

a lithium salt, and

contacting the positive electrode, the negative electrode, and the separator with the electrolyte to manufacture the secondary battery.



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Claims searched: 1-21

Date of search: 21 April 2022

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X	1-18, 21	US 2017/0244135 A1 (MOMO) see paragraphs [0208], [0216]-[0217] and [0224]-[0229] in particular
X	1-18, 21	JP 2013152825 A (SONY CORP) see paragraphs [0055], [0071], [0086]-[0087], [0198], [0214] and [0218] in particular, and also the EPODOC abstract and WPI Abstract Accession No. 2013-M14856
X	1-7, 13-18, 21	WO 2020/047228 A1 (HYDRO QUEBEC) see page 23 lines 4-25 and page 24 lines 30-33 in particular

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
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Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^X :

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H01M

The following online and other databases have been used in the preparation of this search report

WPI, EPODOC, Patent Fulltext, INSPEC, XPESP, SPRINGER, XPAIP, XPIOP



International Classification:

Subclass	Subgroup	Valid From
H01M	0010/0569	01/01/2010
H01M	0004/131	01/01/2010
H01M	0004/485	01/01/2010
H01M	0010/0525	01/01/2010
H01M	0010/42	01/01/2006
H01M	0004/505	01/01/2010
H01M	0004/525	01/01/2010
H01M	0004/58	01/01/2010
H01M	0004/62	01/01/2006
H01M	0004/66	01/01/2006