chemical reactions within the battery proceed more slowly, and in freezing temperatures plating of metallic lithium can occur on a graphite anode (negative electrode) surface.

In addition, temperatures of 45˚C and greater have an effect of reducing the cycle life of the cell due to the degradation of the interfacial layer between the electrode material and the electrolyte called the solid electrolyte interface (SEI). This SEI layer which is usually formed on the anode material surface is responsible for stable operation of a lithium ion battery and the upper limit of 45˚C exists because at greater temperatures the SEI layer tends to decompose resulting in a drastic fade in capacity of the cell.

In light of the above challenges, there is a need to provide new electrode materials and surfaces for lithium ion batteries that are capable of operating at high rates and at high temperatures to extend the range of EV and allow for optimal battery function in portable battery powered devices in wider temperature ranges.

In light of the above challenges, there is a need to provide new electrode materials for lithium ion cells that are capable of operating at high or low temperatures.

Summary

The present disclosure generally provides an electrode having a niobium-containing metal oxide surface, an electrochemical cell comprising the electrode, and the use of the cell, for example in a lithium-ion battery, at elevated or reduced temperatures.

The present inventors have established that high energy densities can be achieved using an electrode materials having a niobium-containing metal oxide surface in a lithium-ion cell even when the cell is cycled at elevated or reduced temperatures. The cell displays excellent capacity retention when repeatedly cycled at elevated or reduced temperatures. Moreover, the cell can be charged and discharged at high C rates at both elevated and reduced temperatures. Thus, a lithium-ion cell comprising an electrode having a niobium-containing metal oxide surface has a greater operational temperature range and shows improved cycle stability and elevated or reduced temperatures in comparison to a typical lithium-ion cell comprising a graphite electrode.

Working electrodes having a niobium-containing metal oxide surface and bulk have favourable lithium diffusion properties, and thus exhibit superior rate performance. Above 1.0 V vs. Li+/Li, the formation of SEI is minimal, which means that lithium will not be lost into side reactions with the electrolyte.

A typical lithium-ion cell comprising a graphite electrode operates below 1 V vs Li+/Li and must undergo an initial formation cycle before the cell is sealed. Typically, this formation cycle takes place at elevated temperature, for example 60 °C, in order to allow rapid formation of the SEI in one cycle and the degassing to occur. This adds signification time and cost to the cell manufacturing process.

In accordance with the present disclosure, the niobium-based metal oxide surface minimises or eliminates SEI formation normally observed on the graphite surface during the initial formation step in lithium-ion batteries during the first charge cycle.

Furthermore, in a full cell against e.g. $LiFePO_4$, $LiN(CF_3SO_2)_2$ (LiTFSI) can be used to replace the more toxic $LiPF_6$ electrolyte salt commonly used in standard commercial electrolytes. Moreover, aluminium can be used as the current collector instead of the more expensive copper while avoiding LiAl alloying potentials (≤0.3 V vs. Li+/Li).

In general, the disclosure provides a method of charging and/or discharging an electrochemical cell, wherein the electrochemical cell comprises a working electrode having a niobium-containing metal oxide surface, and wherein the temperature of the electrochemical cell is 45 °C or more, such as 50 °C or more, 55 °C or more or 60 °C or more.

In general, the disclosure also provides a method of charging and/or discharging an electrochemical cell, wherein the electrochemical cell comprises a working electrode having a niobium-containing metal oxide surface, and wherein the temperature of the electrochemical cell is 10 °C or less, such as 5 °C or less or 0 °C or less.

In one aspect, the present disclosure provides a method of charging an electrochemical cell at a C rate of at least 5C, wherein the electrochemical cell comprises a working electrode having a niobium-containing metal oxide surface, wherein the working electrode comprises a layer of niobium-containing metal oxide disposed on a secondary active electrode material, and the working electrode is an anode during discharge of the electrochemical cell.

In one example of the disclosure, there is provided a method of charging and/or discharging an electrochemical cell, wherein the electrochemical cell comprises a working electrode having a surface layer of niobium-containing metal oxide disposed on a secondary active electrode material, and wherein the temperature of the electrochemical cell is 45 °C or more, such as 50 °C or more, 55 °C or more or 60 °C or more.

In another example of the disclosure, there is provided a method of charging and/or discharging an electrochemical cell, wherein the electrochemical cell comprises a working electrode having a surface layer of niobium-containing metal oxide disposed on a secondary active electrode material, and wherein the temperature of the electrochemical cell is 10 °C or less, such as 5 °C or less or 0 °C or less.

The electrochemical cell may contain a counter electrode and an electrolyte, and optionally the electrodes are connectable to or are in connection with a power supply.

The method of either example may involve charging and/or discharging the electrochemical cell at a C rate of at least 5C, such as at least 10C, at least 20C, at least 30C, at least 40C at least 50C or at least 60C.

The method may involve a cycle of charging and discharging or discharging and charging the electrochemical cell, and the method may comprise 2 cycles or more, 5 cycles or more, 10

cycles or more, 50 cycles or more, 100 cycles or more, 500 cycles or more, 1,000 cycles or more, or 2,000 cycles or more.

The layer of niobium-containing metal oxide may have a maximum thickness of 4.5 nm or less.

The layer of niobium-containing metal oxide may be disposed on a particle of the secondary active electrode material. Alternatively, the layer of niobium-containing metal oxide may be disposed on a film of the secondary active electrode material.

The niobium-containing metal oxide may be selected from the different polymorphs of Nb_2O_5, NbO_2, Nb_2O_3 or combinations thereof.

The niobium-containing metal oxide may be doped with additional elements such as, phosphorus, aluminium, copper, chromium, zirconium, vanadium and lithium.

The niobium-containing metal oxide may be selected from a niobium tungsten oxide, a titanium niobium oxide, a niobium molybdenum oxide, or combinations thereof. Niobium vanadium oxide may also be used as the niobium-containing metal oxide.

The secondary active electrode material may be selected from carbon, silicon or a metal oxide. Lithium and silver may also be used as secondary active electrode materials.

The secondary active electrode material may be selected from graphite, reduced graphite oxide or hard carbon.

The secondary active electrode material may be selected from lithium titanate, titanium tantalum oxide or tantalum molybdenum oxide. Lithium vanadium oxide, lithium titanium silicate and lithium vanadium oxide phases may also be used as secondary active electrode material.

In another aspect, there is provided a working electrode comprising a surface layer of a niobium-containing metal oxide disposed on a secondary active electrode material, wherein the working electrode is an anode during a discharge step of an electrochemical cell and the working electrode is chargeable at a C rate of at least 5C.

In a third example of the disclosure, there is provided an electrode, which may be referred to as a working electrode, having a niobium-containing metal oxide surface. The working electrode is suitable for use as an electrode in a lithium-ion battery.

The working electrode comprises a surface layer of a niobium-containing metal oxide disposed on a secondary active electrode material.

The layer of niobium-containing metal oxide may be disposed on a particle of the secondary active electrode material. Alternatively, the layer of niobium-containing metal oxide may be disposed on a film of the secondary active electrode material.

The niobium-containing metal oxide may be selected from a Nb_2O_5 polymorph, NbO_2, Nb_2O_3 or combinations thereof.

The niobium-containing metal oxide may be doped with additional elements such as, phosphorus, aluminium, copper, chromium, zirconium, vanadium and lithium.

The niobium-containing metal oxide may be selected from a niobium tungsten oxide, a titanium niobium oxide, a niobium molybdenum oxide, or combinations thereof. Niobium vanadium oxide may also be used as the niobium-containing metal oxide.

The secondary active electrode material may be selected from carbon, silicon or a metal oxide. Lithium and silver may also be used as secondary active electrode materials.

The secondary active electrode material may be selected from graphite, reduced graphite oxide or hard carbon.

The secondary active electrode material may be selected from lithium titanate, titanium tantalum oxide and tantalum molybdenum oxide. Lithium vanadium oxide, lithium titanium silicate and lithium vanadium oxide phases may also be used as secondary active electrode material.In another aspect of the disclosure, there is provided an electrochemical cell comprising the working electrode of the disclosure.

In another aspect, there is provided a solid-state battery comprising a working electrode as disclosed herein.

In another example of the disclosure there is provided a lithium-ion battery comprising one or more electrochemical cells of the disclosure. Where there are a plurality of cells, these may be provided in series or parallel.

In another aspect, the present disclosure refers to the use of a working electrode having a niobium-containing metal oxide surface in an electrochemical cell for charging the electrochemical cell at a C rate of at least 5C, wherein the working electrode comprises a layer of niobium-containing metal oxide disposed on a secondary active electrode material and the working electrode is an anode during discharge of the electrochemical cell.

In another example of the disclosure there is provided the use of a working electrode having a surface layer of niobium-containing metal oxide disposed on a secondary active electrode material in an electrochemical cell, wherein the temperature of the electrochemical cell during charging or discharging 45 °C or more, such as 50 °C or more, 55 °C or more or 60 °C or more.In another example of the disclosure there is provided the use of a working electrode having a surface layer of niobium-containing metal oxide disposed on a secondary active electrode material in an electrochemical cell, wherein the temperature of the electrochemical cell during charging or discharging is 10 °C or less, such as 5 °C or less or 0 °C or less.

These and other aspects and examples of the disclosure are described in more detail below.

Summary of the Figures

Figure 1 illustrates a working electrode particle having niobium-containing metal oxide surface layer with an intermediate metal oxide layer (top) and without an intermediate metal oxide layer (bottom).

Figure 2A shows the rate performance of a NWO ($Nb_{16}W_5O_{55}$) /NMC ($LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$) cell as a function of the cell operation temperature at 60 °C (top), 25 °C (middle) and 10 °C (bottom).

Figure 2B shows long-term cycle performance of a NWO/NMC cell at 60 °C under 10C rate.

Figure 2C shows long-term cycle performance of a NWO/NMC cell at 25 °C (top) and 10 °C (bottom) under 5C rate conditions.

Figure 2D shows rate performance comparison of a NWO/LFP cell as a function of temperature at 60 °C (top), 25 °C (middle) and 10 °C (bottom).

Claims

1. A method of charging an electrochemical cell at a C rate of at least 5C, wherein the electrochemical cell comprises a working electrode having a niobium-containing metal oxide surface, wherein the working electrode comprises a layer of niobium-containing metal oxide disposed on a secondary active electrode material, and the working electrode is an anode during discharge of the electrochemical cell.

2. The method of claim 1 wherein the temperature of the electrochemical cell is 45 °C or more, such as 50 °C or more, 55 °C or more or 60 °C or more; or wherein the temperature of the electrochemical cell is 10 °C or less, such as 5 °C or less or 0 °C or less.

3.. The method of any of claims 1 or 2, wherein the layer of niobium-containing metal oxide has a maximum thickness of 4.5 nm or less.

4. The method of any of claims 1 to 3, wherein the niobium-containing metal oxide is selected from a Nb_2O_5 polymorph, NbO_2, Nb_2O_3 or combinations thereof.

5. The method of any of claims 1 to 4, wherein the niobium-containing metal oxide is doped with an element selected from phosphorus, aluminium, copper, chromium, zirconium, vanadium and lithium.

6. The method of any of claims 1 to 3, wherein the niobium-containing metal oxide is selected from a niobium tungsten oxide, a titanium niobium oxide, a niobium molybdenum oxide, a niobium vanadium oxide or combinations thereof.

7. The method of any of claims 1 to 3, wherein the niobium-containing metal oxide is selected from a Nb_2O_5 polymorph, NbO_2, Nb_2O_3 or combinations thereof; or a niobium tungsten oxide, a titanium niobium oxide, a niobium molybdenum oxide, a niobium vanadium oxide or combinations thereof.

8. The method of any of claims 1 to 7, wherein the layer of niobium-containing metal oxide is disposed on a particle of the secondary active electrode material, or the layer of niobium-containing metal oxide is disposed on a film of the secondary active electrode material.

9. The method of any of any preceding claim, wherein the secondary active electrode material is selected from carbon, silicon or a metal oxide.

10. The method of claim 9, wherein the secondary active electrode material is selected from graphite, reduced graphite oxide or hard carbon.

11. The method of claim 9, wherein the secondary active electrode material is selected from lithium titanate, titanium tantalum oxide, tantalum molybdenum oxide and lithium vanadium oxide.

12. The method of any preceding claim, wherein the method is a method of charging an electrochemical cell at a C rate of at least 10C, such as at least 20C, at least 30C, at least 40C at least 50C or at least 60C.

13. The method of any preceding claim, wherein the method comprises a cycle of charging and discharging, or discharging and charging the electrochemical cell, wherein the method comprises 2 cycles or more, 5 cycles or more, 10 cycles or more, 50 cycles or more, 100 cycles or more, 500 cycles or more, 1,000 cycles or more, or 2,000 cycles or more.

14. A working electrode comprising a surface layer of a niobium-containing metal oxide disposed on a secondary active electrode material, wherein the working electrode is an anode during a discharge step of an electrochemical cell and the working electrode is chargeable at a C rate of at least 5C.

15. The working electrode of claim 14, wherein the layer of niobium-containing metal oxide has a maximum thickness of 4.5 nm or less.

16. The working electrode of any one of claims 14 or 15, wherein the niobium-containing metal oxide is selected from a Nb_2O_5 polymorph, NbO_2, Nb_2O_3 or combinations thereof.

17. The working electrode of any of claims 14 to 16, wherein the niobium-containing metal oxide is doped with an element selected from phosphorus, aluminium, copper, chromium, zirconium, vanadium and lithium.

18. The working electrode of any one of claims 14 to 17, wherein the niobium-containing metal oxide is selected from a niobium tungsten oxide, a titanium niobium oxide, a niobium molybdenum oxide, a niobium vanadium oxide or combinations thereof.

19. The working electrode of any of claims 14 to 16, wherein the niobium-containing metal oxide is selected from a Nb_2O_5 polymorph, NbO_2, Nb_2O_3 or combinations thereof; or a niobium tungsten oxide, a titanium niobium oxide, a niobium molybdenum oxide, a niobium vanadium oxide or combinations thereof.

20. The working electrode of any of claims 14 to 19, wherein the layer of niobium-containing metal oxide is disposed on a film of the secondary active electrode material, or the layer of niobium-containing metal oxide is disposed on a particle of the secondary active electrode material.

21. The working electrode of any of claims 14 to 20, wherein the secondary active electrode material is selected from carbon, silicon or a metal oxide.

22. The working electrode of claim 21, wherein the secondary active electrode material is selected from graphite, reduced graphite oxide or hard carbon.

23. The working electrode of claim 21, wherein the secondary active electrode material is selected from lithium titanate, titanium tantalum oxide, tantalum molybdenum oxide and lithium vanadium oxide.

24. An electrochemical cell comprising a working electrode according to any one of claims 14 to 23.

25. A solid-state battery comprising a working electrode according to any one of claims 14 to 23.

26. Use of a working electrode having a niobium-containing metal oxide surface in an electrochemical cell for charging the electrochemical cell at a C rate of at least 5C, wherein the working electrode comprises a layer of niobium-containing metal oxide disposed on a secondary active electrode material and the working electrode is an anode during discharge of the electrochemical cell.

27. Use of a working electrode of claim 26, wherein the temperature of the electrochemical cell during charging or discharging is 45 °C or more, such as 50 °C or more, 55 °C or more or 60 °C or more; or wherein the temperature of the electrochemical cell during charging or discharging is 10 °C or less, such as 5 °C or less or 0 °C or less.