capability and low or zero cobalt content. One of main issues with spinel cathode materials such as LMO (lithium manganese oxide), LNMO (lithium nickel manganese oxide) is the dissolution of manganese divalent ions ($2\ Mn^{3+} \rightarrow Mn^{4+} + Mn^{2+}$) during battery charge process, which mostly occurs at electrode/electrolyte interface, then re-deposition on anode side and destruction of its SEI as through the same mechanism of Ni-rich cathode materials.

To address the interface issues between electrolyte and cathode electrodes such as transition metal dissolution, excessive electrolyte decomposition, thin film deposition on cathodes and/or cathode materials can be applied. For example, US8535832B2 discloses wet coating of metal oxide (Al_2O_3, Bi_2O_3, B_2O_3, ZrO_2, MgO, Cr_2O_3, $MgAl_2O_4$, Ga_2O_3, SiO_2, SnO_2, CaO, SrO, BaO, TiO_2, Fe_2O_3, MoO_3, MoO_2, CeO_2, La_2O_3, ZnO, $LiAlO_2$ or combinations thereof) onto a cathode active material comprising Ni, Mn and Co. US9543581B2 describes dry coating of amorphous Al_2O_3 on precursor particles of cathode active materials comprising Ni, Mn and Co elements. US9614224B2 describes a $Li_xPO_yMn_z$ coating using sputtering method on cathode active materials comprising Mn. US9837665B2 describes lithium phosphorus oxynitride (LiPON) thin films coating using sputtering method on cathode active materials comprising Li, Mn, Ni, and oxygen containing compound with a dopant of at least one of Ti, Fe, Ni, V, Cr, Cu, and Co. US9196901B2 describes Al_2O_3 thin films coating using an atomic layer deposition (ALD) method on cathode laminates and cathode active materials comprising Co, Mn, V, Fe, Si, or Sn and being an oxide, phosphate, silicate or a mixture of two or more thereof. US10224540B2 describes Al_2O_3 thin film coating using ALD method on a porous silicon anode. US10177365B2 describes AlW_xF_y or $AlW_xF_yC_z$ thin film coating onto cathode active materials comprising $LiCoO_2$ using ALD. US9531004B2 describes hybrid thin films coating comprising the first layer of Al_2O_3, TiO_2, SnO_2, V_2O_5, HfO_2, ZrO_2, ZnO, and the second layer of fluoride-based coating, a carbide-based coating, and a nitride-based coating using ALD method on anode materials group consisting of: lithium titanate $Li_{(4+x)}Ti_5O_{12}$, where $0 \leqq x \leqq 3$ (LTO), graphite, silicon, silicon-containing alloys, tin-containing alloys, and combinations thereof.

Brief Summary of the Invention

The disclosure provides the following solutions to form an artificial interphase on an electrode to protect it from fast declining electrochemical behaviors, by depositing Doped-Metal Oxides Layers onto the cathode or cathode active materials by ALD or

CVD. These Doped-Metal Oxides Layers reduce excessive decomposition of electrolyte at the electrode/electrolyte interfaces during SEI formation, reducing capacity loss at the first cycles. The presence of such a Doped-Metal Oxides Layer also reduces the cathode active materials' transition metal cation dissolution, which is caused by parasite reactions between electrolyte and cathode active materials, then its re-deposition, on the anode. Electrochemical activity of the battery is thereby improved. As discussed above, other types of films have been proposed, especially pure metal oxides such as Al_2O_3. However this type of material behaves as an ion-insulator, and therefore does not allow the best electrochemical performance of the resulting cathode and battery. The composition of the Doped-Metal Oxides Layers takes into account the need of the Li ion diffusion, through the choice of transition metals that can undergo a change of oxidation state. The corresponding metal oxide is deposited with separate dopant chemicals and/or using vapor phase metal precursors that contain dopents such as C, Si, Sn, B, Al, N, P, and/or S. The deposition conditions are selected to produce the Doped-Metal Oxides film rather than a metal oxide film. While not wishing to be bound by any specific theory, the Doped-Metal Oxides films would in most circumstances be considered "low quality" films not suitable for most applications. For example, such materials are generally low density due to porosity caused by the dopant elements (especially Carbon and Phosphorus). However it may be such porosity that facilitates a balance between protecting the cathode and allowing Li ion movement. It is also possible that adding first row transition elements, preferably Mn, Ni, Co, Fe, Cu, may increase the films' ion conductivity and thereby improve the electrochemical performance.

In a first aspect, the present disclosure provides a cathode or a cathode active material comprising at least a partial surface coating of a doped metal oxide film, preferably the metal is selected from Niobium, Tantalum, Vanadium, Zirconium, Titanium, Hafnium, Tungsten, Molybdenum, Chromium and combinations thereof, wherein the doped metal oxide has an average atomic composition of $M_xO_yD_z$, wherein M is a transition metal or a II-A to VI-B element, O is oxygen, and D is a dopant atom other than lithium, M or O, preferably D is selected from C, Si, Sn, B, Al, N, P, or S, and wherein x = 10 to 60%, y ranges from 10 to 60%, and z ranges from 10 to 30%.

In a second aspect, the present disclosure provides a proton exchange membrane battery comprising a cathode or cathode active material according to the first aspect.

In a third aspect, the present disclosure provides a method of coating a cathode or a cathode active material with a doped metal oxide film, the method comprising the steps of: a1. exposing the cathode or cathode active material to a chemical precursor vapor, and b1. depositing the doped metal oxide film on the cathode or cathode active material, wherein the doped metal oxide has an average atomic composition of $M_xO_yD_z$, wherein M is a transition metal or a II-A to VI-B element, O is oxygen, and D is a dopant atom other than lithium, M or O, preferably D is selected from C, Si, Sn, B, Al, N, P, or S, and wherein x = 10 to 60%, y ranges from 10 to 60%, and z ranges from 10 to 30%.

The disclosure may be further understood in relation to the following non-limiting, exemplary embodiments described as enumerated sentences:

1. A cathode or a cathode active material comprising at least a partial surface coating of a doped metal oxide film, preferably the metal is selected from Niobium, Tantalum, Vanadium, Zirconium, Titanium, Hafnium, Tungsten, Molybdenum, Chromium and combinations thereof.
2. The cathode or a cathode active material of SENTENCE 1, wherein the doped metal oxide film is either a metal, oxygen and carbon-containing film or a metal, oxygen and phosphorus containing film.
3. The cathode or a cathode active material of SENTENCE 1, wherein the doped metal oxide film is a doped Niobium oxide film.

CLAIMS

1. A cathode or a cathode active material comprising at least a partial surface coating of a doped metal oxide film, preferably the metal is selected from Niobium, Tantalum, Vanadium, Zirconium, Titanium, Hafnium, Tungsten, Molybdenum, Chromium and combinations thereof, wherein the doped metal oxide has an average atomic composition of $M_xO_yD_z$, wherein M is a transition metal or a II-A to VI-B element, O is oxygen, and D is a dopant atom other than lithium, M or O, preferably D is selected from C, Si, Sn, B, Al, N, P, or S, and wherein x = 10 to 60%, y ranges from 10 to 60%, and z ranges from 10 to 30%.

2. The cathode or a cathode active material of claim 1, wherein the doped metal oxide film is either a metal, oxygen and carbon-containing film or a metal, oxygen and phosphorus containing film.

3. The cathode or a cathode active material of claim 1, wherein the doped metal oxide film is a doped Niobium oxide film.

4. The cathode or a cathode active material of claim 1, wherein the doped metal oxide film is a Niobium, oxygen and carbon-containing film or a Niobium, oxygen and phosphorus containing film.

5. The cathode or a cathode active material of any of claims 1-4, wherein the cathode or a cathode active material is only partially coated with the doped metal oxide film.

6. The cathode or a cathode active material of claim any of claims 1-5, wherein the doped metal oxide film has an average thickness of 0.02 nm to 10nm, preferably 0.1 nm to 5nm, most preferably 0.2 to 2 nm.

7. The cathode or a cathode active material of any of claims 1-4, wherein the doped metal oxide film has an atomic percentage for carbon atoms from 15 to 25%.

8. The cathode or a cathode active material of claim any of claims 3-7, wherein the

doped metal oxide film has a refractive index of 1.5 to 2.5, preferably 1.6 to 2.1, most preferably 1.7 to 2.0.

9. A proton exchange membrane battery comprising a cathode or cathode active material according to any of claims 1-8.

10. A method of coating a cathode or a cathode active material with a doped metal oxide film, the method comprising the steps of:

a1. exposing the cathode or cathode active material to a chemical precursor vapor, and

b1. depositing the doped metal oxide film on the cathode or cathode active material,

wherein the doped metal oxide has an average atomic composition of $M_xO_yD_z$, wherein M is a transition metal or a II-A to VI-B element, O is oxygen, and D is a dopant atom other than lithium, M or O, preferably D is selected from C, Si, Sn, B, Al, N, P, or S, and wherein x = 10 to 60%, y ranges from 10 to 60%, and z ranges from 10 to 30%.

11. The method of claim 10, further comprising a step a2. of exposing the cathode or cathode active material to a co-reactant.

12. The method of claim 11, wherein the step a1. of exposing the cathode or cathode active material to a chemical precursor vapor and the step a2. of exposing the cathode or cathode active material to a co-reactant, are sequentially performed.

13. The method of claim 12, further comprising a step a1i. of purging the chemical precursor vapor prior to step a2. of exposing the cathode or cathode active material to a co-reactant.

14. The method of claim 13, wherein the step b1. depositing the doped metal oxide film on the cathode or cathode active material comprises an atomic layer deposition step.

15. The method of claim 13, wherein the step b1. of depositing the doped metal oxide film on the cathode or cathode active material comprises a chemical vapor deposition

step.

16. The method of claims 10-15, wherein the co-reactant is an oxygen source such as O2, O3, H2O, H2O2, NO, NO2, N2O or a NOx; an oxygen-containing silicon precursor, an oxygen-containing tin precursor, a phosphate such as trimethylphosphate, diethyl phosphoramidate, or a sulfate.

17. The method of any of claims 10-16, wherein one or more of steps are repeated.

18. The method of any of claims 10-17, wherein a temperature of the chemical precursor vapor and/or the cathode or cathode active material is 200 degrees C or less, preferably 50 degrees C to 200 degrees C, more preferably 100 degrees C to 150 degrees C.

19. The method of any of claims 10-18, wherein the cathode active material, or the cathode active material in the cathode, is selected from the group consisting of a) layered oxides such as Ni-rich cathode materials like NMC (lithium nickel manganese cobalt oxide) and NCA (lithium nickel cobalt aluminum oxide); b) spinel cathode materials such as LMO (lithium manganese oxide), LNMO (lithium nickel manganese oxide); c) Olivine structured cathode materials, in particular the family of Olivine phosphates such as LCP (lithium cobalt phosphate), LNP (lithium nickel phosphate); and combinations thereof.