

ited to, Sr^{2+} , which have E_{Red}^{ϕ} values of -2.958 V (assuming $\gamma=1$) versus a standard hydrogen potential. The lower activity of these cations can result in an effective ERP lower than that of Li^+ ions. The larger size and higher charge should be accounted for in the non-aqueous electrolyte. Lithium films were deposited using the control electrolyte along with electrolytes comprising $0.05\text{ M Sr}(\text{PF}_6)_2$. Deposition from the electrolyte comprising 0.05 M Sr^{2+} results in a lithium film that is smooth, free of dendrites, and void of Sr in/on the anode. This again indicates that the activity coefficient for Sr^{2+} in these solutions is less than unity.

Using this approach, C2 cations of the surface-smoothing additive are not reduced and deposited on the substrate. The C2 cations are not consumed because these cations exhibit an effective reduction potential lower than that of the reactant. In contrast, traditional electrodeposition can utilize additives having a reduction potential higher than that of the reactants; therefore, they will be reduced during the deposition process and “sacrificed or consumed,” for example, as part of an SEI film or as an alloy to suppress dendrite growth. As a result, the additive concentration in the electrolyte will decrease with increasing charge/discharge cycles and the effect of the additives will quickly degrade. In contrast, the C2 cations described herein will form a temporary electrostatic shield or “cloud” around the dendritic tips that retards further deposition of C1 in this region. This “cloud” will form whenever a protrusion is initiated, but it will dissipate once applied voltage is removed or the protrusion is eliminated. Accordingly, in some embodiments, the applied electrical potential is of a value that is less than, or equal to, the ERP of the reactants and greater than the effective ERP of the cations of C2.

Lithium films having an SEI layer on the surface and deposited using electrolytes comprising 0.05 M Cs^+ , Rb^+ , K^+ , or Sr^{2+} additives were analyzed by x-ray photoelectron spectroscopy (XPS), Energy-dispersive X-ray spectroscopy (EDX) dot mapping, and Inductively coupled plasma atomic emission spectroscopy (ICP/AES) methods. XPS and EDX results did not show Cs, Rb, K, and Sr elements in the SEI films within the detectable limits of the analysis instruments. In addition, ICP-AES analysis did not identify Cs, Rb, K, and Sr elements in the bulk of deposited lithium film (including the SEI layer on the surface) within detectable limits.

Dendrite formation is not only a critical issue in rechargeable lithium metal batteries, but also an important issue in high power lithium ion batteries because lithium metal dendrites can grow at the anode surface when the lithium ions cannot move quickly enough to intercalate into the anode, which can comprise graphite or hard carbon, during rapid charging. In this case, the lithium dendrites can lead to short circuits and thermal runaway of the battery. Accordingly, a carbonaceous anode is described herein to demonstrate suppression of lithium dendrite growth in a lithium ion battery. FIG. 6 compares the optical (6A and 6D) and SEM images (6B, 6C, 6E, and 6F) of lithium particles formed on the hard carbon anode after it was charged to 300% of its theoretical capacity in a control electrolyte (without additives) and in an electrolyte having a surface smoothing additive comprising 0.05 M CsPF_6 . A significant amount of lithium metal was deposited on the surface of carbon electrode (see grey spots in FIG. 6A) for the sample overcharged in the control electrolyte. FIGS. 6B and 6C show clear dendritic growth on the electrode surface. In contrast, no lithium metal deposition was observed on the surface of carbon electrode (see FIG. 6D) for the sample overcharged in the electrolyte with 0.05 M Cs^+ additive (the white line on the bottom of the carbon sample is due to an optical reflection). After removing a small piece of carbon from the sample (see the circled area in FIG. 6D), it

was found that excess lithium was preferentially grown on the bottom of the carbon electrode as shown in FIGS. 6E and 6F.

While a number of embodiments of the present invention have been shown and described, it will be apparent to those skilled in the art that many changes and modifications may be made without departing from the invention in its broader aspects. The appended claims, therefore, are intended to cover all such changes and modifications as they fall within the true spirit and scope of the invention.

We claim:

1. A method for improving surface smoothness during electrodeposition of a first conductive material (C1) on a substrate surface, the method comprising:

providing an electrolyte solution comprising reactants from which C1 is synthesized and a soluble, surface-smoothing additive comprising cations of a second conductive material (C2), wherein cations of C2 have a) a standard electrical reduction potential that is greater than an electrochemical reduction potential of the reactants and (b) an activity in solution such that an effective electrochemical reduction potential of the cations of C2 in the solution is lower than the electrochemical reduction potential of the reactants; and

applying an electrical potential that is less than the electrochemical reduction potential of the reactants and greater than the effective electrochemical reduction potential of the cations of C2, thereby reducing the reactants and forming C1 on the substrate surface.

2. The method of claim 1, further comprising:

accumulating cations of C2 at protrusions on the substrate surface, thereby forming an electrostatically shielded region near each protrusion; and temporarily repelling reactants from the electrostatically shielded region near each protrusion.

3. The method of claim 1, wherein C1 is a metallic material and the reactants comprise cations of C1.

4. The method of claim 3, wherein C1 is selected from a group consisting of Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, Al, Ga, In, Tl, Ge, Sn, Pb, As, Sb, Bi, Se, Te, Bi, Po, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, W, Pt, Au, Hg, and combinations thereof.

5. The method of claim 3, wherein C1 comprises Li.

6. The method of claim 1, wherein C1 comprises an electronic conductive polymer and the reactants comprise monomers of the polymer.

7. The method of claim 1, wherein the cations of C2 are metal cations.

8. The method of claim 7, wherein the cations of C2 comprise a metal selected from a group consisting of Li, Cs, Rb, K, Ba, La, Sr, Ca, Ra, Zr, Te, B, Bi, Ta, Ga, Eu, S, Se, Nb, Na, Mg, Cu, Al, Fe, Zn, Ni, Ti, Sn, Sb, Mn, V, Ta, Cr, Au, Ge, Co, As, Ag, Mo, Si, W, Ru, I, Fc, Br, Re, Bi, Pt, Pd, and combinations thereof.

9. The method of claim 1, wherein the cations of C2 have a concentration in the electrolyte solution that is less than 10% of that of the reactants.

10. The method of claim 1, wherein the concentration of the cations of C2 have a concentration in the electrolyte solution that is less than, or equal to, 5% of that of the reactants.

11. The method of claim 1, wherein the surface-smoothing additive comprises an anion selected from a group consisting of PF_6^- , AsF_6^- , BF_4^- , $\text{N}(\text{SO}_2\text{CF}_3)_2^-$, $\text{N}(\text{SO}_2\text{F})_2^-$, CF_3SO_3^- , ClO_4^- , I^- , Cl^- , OH^- , NO_3^- , SO_4^{2-} , and combinations thereof.

12. The method of claim 1, wherein the substrate is an electrode.