Redox Layer Deposition of Thin Films of MnO₂ on Nanostructured Substrates from Aqueous Solutions

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ABSTRACT: In this work we report a new method for depositing thin films of MnO₂ on planar and complex nanostructured surfaces, with high precision and conformality. The method is based on repeating cycles of adsorption of an unsaturated alcohol on a surface, followed by its oxidation with aqueous KMnO₄ and formation of thin, solid MnO₂. The amount of manganese oxide formed in each cycle is limited by the quantity of the adsorbed alcohol, thus the growth exhibits the self-limiting characteristics of Atomic Layer Deposition (ALD). Contrary to the typical ALD, however, the new redox layer deposition (RLD) is performed in air, at room temperature, using common chemicals and simple laboratory glassware, which greatly reduces its cost and complexity. We also demonstrate application of the method for the fabrication of a nanostructured MnO₂/Ni electrode, which was not possible with thermal ALD due to the rapid decomposition of gaseous precursor on the high surface area substrate. Thanks to its simplicity, the conformal deposition of MnO₂ can be easily upscaled and thus exploited for its numerous (electro)chemical applications.

INTRODUCTION

Manganese oxides (MnO_x, $x \in [1, 2]$) are abundant, inexpensive and environmentally-friendly materials used in many industrial applications. Thanks to its attractive electrochemical properties, manganese dioxide (MnO₂) is broadly utilized as a cathode material in lithium-ion and zinc-manganese oxide batteries, as well as being one of the most promising electrode material for supercapacitors.^{1–4} In microelectronics, a few nanometer-thick MnO_x film has been demonstrated as an excellent Cu-diffusion barrier layer.⁵ Manganese oxides also have many catalytic applications in, for example, electro-oxidation of water⁶ and decomposition of nitrogen oxides,⁷ ozone⁸ or formaldehyde.⁹

Conformal deposition of thin films of manganese oxides on high aspect ratio structures is crucial for their integration in the nanostructured devices such as microbatteries or transistors, as well as on the nanostructured, high surface area catalysts supports. Traditionally, the highest conformality of deposited materials can be obtained by means of atomic layer deposition (ALD), which also allows a sub-nanometer thickness control. Classically, ALD consists of sequential exposures of gaseous precursors to the substrate surface, which individually react with the surface in a self-limited manner.^{10–13} This self-limiting aspect is key, as it enables the conformality and atomic level thickness control that have made ALD an indispensable tool in, for example, the semiconductor industry. Thermal and plasma-enhanced ALD has been demonstrated for various manganese oxides, such as MnO (e.g. Burton *et al.*),¹⁴ MnO₂ (e.g. Nilsen *et al.*)^{15,16} and intermediate oxides with controlled Mn oxidation state (e.g. Mattelaer *et al.*).^{17,18} The oxide with the largest number of applications – MnO₂ – has only been reported using

Mn(thd)₃ as a manganese precursor and ozone as an oxidant. However, two major pitfalls exist with this process. On the one hand, the Mn(thd)₃ is a solid at room temperature. Thus, its source needs to be heated to high temperature to obtain only a limited vapor pressure, which possess a serious challenge towards upscaling. Secondly, since the as-grown MnO₂ is also a catalyst for ozone decomposition, ALD of MnO₂ on nanostructured substrates with large surface area may be unfeasible, as suggested by the reports on this ALD process.^{8,15,17} Furthermore, both the thermal- and plasma-ALD processes are vacuum techniques performed at elevated temperatures, requiring costly and reactive metalorganic precursors and a sophisticated, thermally isolated vacuum equipment – implying a high processing cost. While Cure *et al.* recently showed the growth of manganese oxides at room temperature and partially in a liquid phase, this approach still required a dedicated synthesis of the metalorganic precursor (MnAmd₂), the processing in anhydrous toluene, in neutral gas environment and utilization of oxygen plasma.¹⁹ Similarly, some solution-based ALD processes were previously described for other oxides, such as TiO₂ or MgO, but they were always limited by the need of controlled, neutral gas environment and partially anhydrous conditions.^{20,21}

In our approach, we avoided the challenges posed by the classical ALD processes by using aqueous solutions of common KMnO₄ as the manganese precursor and a surface-adsorbing alcohol as the permanganate reducer (Figure 1). Reduction of permanganate ions by alcohols is a textbook example of a redox reaction, which in neutral pH can be written in a simplified form as:

Figure 1. Concept of an RLD cycle

with the standard reduction potentials of $U^\circ_{(1)} = 0.60$ V and $U^\circ_{(2)} = -0.77$ V (assuming $\text{R} = \text{CH}_3$) and thus the standard Gibbs free energy of reaction (3) $\Delta G^\circ_{(3)} \approx -470$ kJ/mol.

The amount of precipitated MnO_2 is determined by the amount of oxidizable groups in the alcohol molecule (OH, C=C etc.) and, importantly in our case, by the amount of alcohol molecules accessible to permanganate ions. Thus, if the quantity of alcohol is limited to a thin layer adsorbed on a solid surface, the as-formed MnO_2 will also be confined to the thin surface layer. A similar mechanism is partially responsible for the brown MnO_2 stains commonly observed on the glassware after handling aqueous KMnO_4 , which readily reacts with trace organic contaminants adsorbed on the glass surfaces. In our case, we used this phenomenon to grow thin films of MnO_2 in a well-controlled manner on planar substrates of transition metals and their oxides, and on complex 3D-nanostructured nickel scaffolds.

To initiate the growth of manganese oxide, propargyl alcohol (PA) was selected as the surface-selective growth precursor. This acetylenic alcohol is a renowned corrosion inhibitor for Ni, Cu, Fe and steel, thanks to its strong tendency for adsorption on metallic surfaces via π -orbitals of the sp-carbon triple bond.^{22–25} Numerous studies on inhibitory effects of PA during acidic corrosion of metals indicated different possible modes of adsorption of PA on metal surfaces, including formation of multilayer polymeric films (observed in hot, acidic environment and long exposure time),^{26,27} formation of non-polymeric multilayers stabilized by π - and hydrogen-bonding,²⁸ or a monolayer adsorption (more plausible during short exposure at room temperature), with a possible conversion to allyl alcohol, as depicted in Figure 1.^{24,29,30} The mechanisms of reaction of permanganate ions with propargyl and allyl alcohol are also complex in nature and depend on multiple parameters such as pH or the alcohol-oxidant ratio. Based on the available literature data, for the current case (neutral pH, low alcohol-permanganate ratio, limited exposure time) we can assume 6-electron oxidation to glycolic and formic acid (for PA)³¹ and either 2-electron oxidation to glycerol or 4-electron oxidation to dihydroxyacetone (for allyl alcohol),^{32–36} with a simultaneous precipitation of MnO_2 (for reaction equations, see Supporting Information). Thus, the general deposition reaction can be written as:

where A_{ads} is the alcohol adsorbed on the surface, $\text{P}_{(\text{aq})}$ is the product or products of its oxidation and $x \in \{6, 4, 2\}$, depending on the number of electrons involved in oxidation of the alcohol.

Our new redox layer deposition (RLD) method eliminates the need for sophisticated equipment and costly precursors to cover complex surfaces with MnO_2 of controllable thickness and excellent conformality. To the best of our knowledge, it is also the first demonstration of an ALD-like deposition

of a metal oxide performed entirely in aqueous phase. This makes the RLD of MnO_2 promising for upscaling, and could potentially enable applications on a larger scale than accessible through classical ALD.

RESULTS

The growth of manganese oxide was investigated on Ni-coated TiN/Si wafers, having a surface root mean squared roughness of 1.2 nm. Prior to deposition, the wafers were ultrasonically cleaned in acetone and isopropyl alcohol to remove any physisorbed organic contaminants, leaving Ni surface covered with a ~ 1 nm thick layer of native NiO / $\text{Ni}(\text{OH})_2$.^{37,38} Each RLD cycle consisted of immersing the wafers in aqueous 0.1 M propargyl alcohol for 1 min, followed by washing for 5 seconds under a stream of deionized water, immersion in 0.1 M KMnO_4 for 1 min and again washing with water. The entire deposition process required only two glass cylinders and a running water source (Figure S1).

Visual inspection of the wafers revealed that the sample color turns brown with an increasing number of deposition cycles, indicating increasing thickness of the deposited manganese oxide (as confirmed below). The structural changes of the surface were investigated using scanning electron microscopy (SEM) (Figure 2). After 5 RLD cycles (Fig. 2b), the Ni surface was covered with closely packed manganese oxide nanoclusters, visibly roughening the original nickel surface (Fig. 2a). After 15 cycles (Fig. 2c), the nickel substrate was covered with a closed layer of deposited material which masked the grainy topography of the Ni surface. Complete coverage of the nickel surface was also indicated by linear scan voltammetry in 1 M KOH, where the sample after 15 deposition cycles no longer showed the nickel surface oxidation peak, as compared to the pristine nickel sample (Figure S2) – indicating no direct contact of the electrolyte to the underlying Ni. After 35 RLD cycles (Fig. 4d and Figure S3), the manganese oxide layer adapted a 3D sheet-like morphology (notice the white edges of the sheets on top of the wafer in Figs. 4d and S3 due to their charging with SEM electrons; see also Fig. 3a below for high magnification image), which is commonly observed in the rich family of MnO_x polymorphs.^{39–42} Such morphology of the layer could be a result of partial solubilization of the film,⁴³ a different packing density of precursor molecules on certain faces of the growing MnO_x layer or a high aspect ratio of the seed crystals generated at the beginning of deposition.^{44,45} Furthermore, the sheet-like morphology could also arise due to a side reaction between PA molecules and the manganese oxide deposited during the previous deposition cycle.⁴⁶

followed by removal of the loose $\text{Mn}(\text{OH})_2$ during the washing step. Although oxidation of unsaturated alcohols with MnO_2 typically requires more than 1 h of exposure time, vigorous shaking and nearly anhydrous conditions (in this case excess of water results in deactivation of MnO_2),⁴⁶ a small degree of this reaction could nevertheless occur between the PA molecules

Figure 2. SEM cross-sectional images (45° tilt) of Ni/TiN/Si wafer surface before (a) and after (b-d) increasing number of RLD cycles: (b) 5, (c) 15, (d) 35 cycles.

Figure 3. TEM images of the layer after 35 RLD cycles. (a) Top wafer surface, (b) High magnification image of the MnO₂ nanosheet, together with FFT image of the selected area, (c) EDX-STEM mapping of the wafer surface for Ni (green), Mn (yellow) and O (red).

in 0.1 M solution and the as-deposited manganese oxide, forming point defects in the coating layer. Acting as natural nucleation sites, these defects could promote the 3D morphology of the layer observed after higher number of deposition cycles.

Transmission electron microscopy (TEM) revealed that the manganese oxide nanosheets are generally amorphous, yet contain a number of small crystallites (Figure 3a-b). Some of those crystallites appear as randomly oriented layers while the others possess tetragonal or cubic symmetry, as observed using Fast Fourier Transform (FFT) analysis. The d-spacing calculated from the FFT patterns equals ~ 2.15 Å, which is close to the spacing value of 2.22 Å for (200) planes of cubic MnO, 2.20 Å for (200) planes of tetragonal β -MnO₂ and 2.01-2.06 Å for (400) planes of cubic λ -MnO₂.⁴⁷ Elemental analysis using energy-dispersive X-ray spectroscopy (EDX-STEM) showed that the composition of the material equals K_{0.05}Mn_{0.90}O₂ which is very close to the nominal stoichiometry of MnO₂ (Figure 3c and Figure S4). The presence of potassium in the film is an effect of thermodynamically-driven entrapment of aqueous K⁺ ions during rapid precipitation of MnO₂.⁴⁸ We can note that the point of zero charge of MnO₂ is typically reported to lay between pH 3 and 7⁴⁹ (in our case, likely at pH ~ 4.5)⁵⁰ while the MnO₄⁻ solution in the vicinity of the growing MnO₂ is slightly alkaline due to the OH⁻ by-products (as in Reaction 3), which makes the surface of the growing MnO₂ negatively charged and thus attractive towards K⁺ adsorption and occlusion. Therefore, it is possible that the level of K impurity could be decreased by using slightly acidic KMnO₄ solution, provided that the pH is still high enough to avoid direct reduction of MnO₄⁻ to water-soluble Mn²⁺.

The chemical state of the layer was also investigated using X-ray Photoelectron Spectroscopy (XPS) (Figure 4). The Mn 2p spectrum exhibits 2p_{3/2} and 2p_{1/2} peaks centered at 642.4 eV and 654.2 eV, respectively, with an additional shoulder below 640 eV. Due to the existence of numerous multiplets in the 2p_{3/2} region, quantification of manganese oxidation state by deconvolution of 2p peaks can be difficult.⁵¹⁻⁵³ While a 2p_{3/2} shoulder at low binding energy indicates the presence of manganese in a lower oxidation state, the maximum of the 2p_{3/2} peak at 642.4 eV and the spin-orbital separation of 2p_{3/2} and 2p_{1/2} peaks of 11.8 eV indicate predominance of the Mn^{IV}O₂ stoichiometry.^{54,55} Furthermore, the O 1s spectrum can be fitted with three peaks centered at 529.8 eV, 531.2 eV and 532.6 eV, corresponding to the oxygen in the oxide (Mn-O-Mn), hydroxide (both Mn-OH and

Ni-OH or defective Ni-O of the substrate) and physisorbed water, respectively.^{51,56} Also in this case, both the separation between the lowest O 1s component and the Mn 2p_{3/2} maximum of 112.6 eV, and the background-corrected intensity ratio of these two peaks of 1.15, agree well with the values reported for MnO₂.^{17,55,57} The XPS spectrum of the underlying Ni shows an expected combination of metallic nickel and its hydrated oxides (Figure S5).

The growth mechanism of the layer was investigated in a series of experiments. First, we investigated the initial stage of the growth using cyclic voltammetry (CV), which is a highly sensitive technique for detecting redox-active materials down to sub-monolayer quantities. Following the cleaning, three Ni samples were processed as follows: the first (reference) sample was held in deionized water for 1 min; the second sample was subjected to one full RLD cycle (1 min in 0.1 M PA and 1 min in 0.1 M KMnO₄); the third sample was held for 1 min in H₂O and then for 1 min in 0.1 M KMnO₄ (thus no PA was used in this case). After the processing, each sample was washed with water and analyzed with CV in 0.5 M Na₂SO₄.

The voltammograms are presented in Figure 5a. The reference Ni sample showed a negligible cathodic current during the initial scan in the negative potential direction, as visible in the inset of Figure 5a. The following positive scan showed an anodic shoulder at 0.20 V vs. AgCl/Ag, followed by an anodic tail at higher potentials. However, the voltammogram recorded during the second CV cycle shows no anodic current besides of that at the upper end of the potential range. Such behavior is typical to the irreversible oxidation of Ni and densification of the native nickel oxide/hydroxide layer present at the nickel surface.⁵⁸

The voltammogram of the sample processed with a full RLD cycle shows a distinct pair of cathodic and anodic peaks at 0.05 V and 0.34 V vs. Ag/AgCl, respectively. This pair of peaks can be ascribed to the partially reversible reduction of MnO₂ to MnOOH:⁵⁹

The integrated charge of the cathodic peak was separately confirmed to scale with the number of RLD cycles (Figure S6), showing it reflects the increasing presence of MnO₂. Interestingly, the sample processed in water and KMnO₄ (without PA) showed the same pair of MnO₂/MnOOH redox peaks, although the integrated cathodic charge was 15% smaller than for the sample processed with a full RLD cycle, indicating lower amount of deposited material. The presence of MnO₂ on the sample treated in water and KMnO₄ can be explained by the nucleation of MnO₂ from the redox reaction of permanganate ions with the nickel surface:

and

The spontaneity of these reactions is dictated by the large difference in the reduction potentials (U) of the MnO₄⁻/MnO₂ and NiO/Ni or Ni(OH)₂/Ni redox pairs (at pH = 7 and KMnO₄ concentration of 0.1 M, $\Delta U_{(7a)} = 1.43$ V and $\Delta U_{(7b)} = 1.41$ V), translating into the Gibbs free energy of Reactions 7a and 7b of -818 kJ/mol and -829 kJ/mol, respectively (for detailed calculations, see Supporting Information). Although the pristine Ni surface is already partially protected by a thin native nickel oxide/hydroxide layer, nickel oxidation can proceed further up to a limiting thickness, as evident from the reference experiment. The similarity of the samples processed in

Figure 4. XPS spectra of MnO₂ layer on Ni wafer. (a) Mn 2p spectrum, (b) O 1s spectrum.

Figure 5. Growth dynamics of the layer. (a) Cyclic voltammograms of Ni samples after 1 min of immersion in H_2O (reference), 1 min in $\text{H}_2\text{O} + 1$ min in KMnO_4 and 1 min in PA + 1 min in KMnO_4 (1 RLD cycle), (b) Growth on Ni after 5-35 deposition cycles using PA or water, (c) Growth per cycle vs. immersion time in PA, (d) Growth on different substrates. The voltammograms in (a) were recorded in 0.5 M Na_2SO_4 at 10 mV/s. The dashed lines in (b) represent the linear fit of GPC to the number of RLD cycles; the dashed line in (c) represents the fit of GPC to Equation 9 (fitted parameters are also displayed); the lines in (d) are non-fitted guides to the eye. The units of annotated GPC in (d) are atoms of Mn / (nm^2 cycle). Note that although the GPC at $t = 0$ in (c) is 30% lower than the background GPC in (b), the difference is close to the statistical error.

$\text{H}_2\text{O}/\text{KMnO}_4$ and PA/KMnO_4 shows that in the first RLD cycle, deposition of MnO_2 is dominated by the redox reaction between the metal surface and permanganate ions, which can happen simultaneously to the oxidation of the adsorbed PA.

The growth of the layer was further investigated after 5 - 35 RLD cycles. The quantity of MnO_2 on Ni was determined using X-ray Fluorescence spectroscopy (XRF) calibrated with Rutherford Backscattering Spectrometry (RBS) (Figure 5b). The amount of manganese on the wafers processed with RLD was found to increase linearly with the number of RLD cycles ($R^2 = 0.997$), with a growth rate of 3.9 ± 0.2 at Mn/nm^2 per cycle. In a control experiment, when water was used instead of propargyl alcohol, the growth was less linear ($R^2 = 0.988$) and the growth rate diminished by 60% to 1.5 ± 0.2 at Mn/nm^2 per cycle. The growth of manganese oxide in this case is due to the slow decomposition of MnO_4^- , which is catalyzed by the MnO_2 formed in the first cycle (Reaction 7):

Although the self-decomposition of MnO_4^- is known to occur extremely slowly without extra irradiation with light (in our case, at the rate of $\sim 4 \times 10^{-12}$ mol/ cm^2 per s of immersion in KMnO_4), its influence is nevertheless detectable at the atomic scale.^{60,61}

The significantly higher growth rate of the manganese oxide formed with propargyl alcohol indicates that the PA molecules can strongly adsorb on the surface of as-formed MnO_2 , facilitating continuous deposition of the layer. Consequently, the rate of the deposition is determined by the PA adsorption and the reaction of the adsorbed alcohol with MnO_4^- . Previous

studies already showed that the reactions of permanganate ions with PA and allyl alcohol are kinetically fast and can complete in about 15 seconds.^{31,62,63} Thus, we investigated the effect of immersion time of the samples in propargyl alcohol solution on the overall growth per cycle (GPC) of the layer, keeping the other parameters of the deposition unchanged (Figure 5c). The GPC was found to saturate at 60 s of immersion, with no significant changes after the longer exposure times. Such saturation behavior indicates a self-limiting type of growth, characteristic for ALD processes. That kind of growth is typically due to strong, monolayer adsorption of the growth precursors, although in our case it could be additionally affected by the equilibrium between MnO_2 deposition and its consumption in the side reaction with PA (Reaction 5). Indeed, the samples subjected to 120 s of immersion in PA had visibly non-uniform coating (also resulting in a larger error of the GPC – as visible in Fig. 5c), which could be due to a partial dissolution of MnO_2 due to its reaction with propargyl alcohol.

Despite the complexity of the deposition, in the analyzed conditions the RLD closely follows the kinetics of an adsorption-driven growth, which can be described by a Lagergen-like equation (dashed line in Fig. 5c):⁶⁴⁻⁶⁶

$$\text{GPC} = \text{GPC}_{\text{sat}}(1 - e^{-at}) + b \quad (9)$$

where GPC is the observed growth per cycle, GPC_{sat} is the saturated (limiting) growth per cycle, t is the time of immersion of samples in PA and a is the parameter describing dependence of GPC on temperature.⁶⁵ In our case, we include the constant b to account the contribution of the background decomposition of MnO_4^- to the overall GPC (Reaction 8). Thus, in

the saturation regime, the GPC_{sat} can be considered as the growth rate dictated by the presence of the adsorbed alcohol. Fitting the experimental data to Equation 8 gave GPC_{sat} value of 3.1 ± 0.1 at Mn/nm² per cycle. According to the possible stoichiometries of the deposition reaction (Equation 4), such GPC corresponds to the oxidation of 1.6-4.7 molecules of adsorbed alcohol per nm² in each deposition cycle, which is in a reasonable agreement with the previously reported monolayer capacity of propargyl alcohol of 3.6 molecules/nm².^{22,67} Furthermore, the sum of the fitted GPC_{sat} and b gives the total GPC of 4.1 at Mn/nm² per cycle in the saturation regime. If the porosity of the layer is neglected, this GPC corresponds to the equivalent growth rate of 1.2 ± 0.2 Å/cycle of dense MnO₂ (taking into account the average crystal density of MnO₂ polymorphs of 4.74 ± 0.48 g/cm³).⁶⁸ Such growth rate remains below the MnO₂ monolayer thickness (about 0.2 – 0.7 nm),^{68–70} while being significantly higher than the saturation GPC for thermal ALD of MnO₂ (0.15–0.3 Å/cycle).^{15,17} The low GPC of the thermal ALD has been previously ascribed to the steric hindrance of the large metalorganic precursor molecules adsorbed during the first half-cycle (for example, surface footprint of Mn(thd)₂ equals ~150 Å²).^{15,17} In our case, the small size of PA molecules (surface footprint of 32 Å²)⁶⁷ and hydrated MnO₄⁻ ions (cross section of ~37 Å²)⁷¹ allows higher density of deposition sites at the surface, substantially increasing the achievable growth rates.

While in the saturation regime a complete ALD cycle takes less time (e.g. 49 s)¹⁷ as compared to the RLD cycle in the analyzed conditions (130 s), thanks to a higher growth rate the RLD allows a faster growth (equivalent of 0.55 Å/min) compared to the reported ALD (0.18–0.37 Å/min, depending on growth temperature, reactor type and dimensions). Note here that the RLD can be performed at room temperature, while the reported ALD can only be done above 150 °C and involves sublimation of hard-to-vaporize solid precursors which limits the scalability of thermal ALD. However, thermal ALD remains to hold advantages in terms of crystallinity and compactness of thicker MnO₂ layers. This is to be expected for several reasons. First, a higher temperature during MnO₂ synthesis is known to improve the crystallinity of the material (compare crystalline γ -MnO₂ prepared electrolytically at 90 °C to the mostly amorphous MnO₂ prepared with the same method at room temperature).⁷² Second, thermal ALD is truly controlled with a single atomic layer precision – e.g. for the ALD of MnO₂, the first sub-cycle forms the Mn layer while the second sub-cycle gives the O layer (note that each step is done until saturation of the sterically-available reactive sites). Together with the higher mobility of gaseous precursor molecules at the higher processing temperature, this allows for better equilibration of the Mn-O arrangement and, eventually, better compactness of the layer. On the other hand, the formation of MnO₂ in the RLD happens only in the second sub-cycle, in a series of dynamic, spontaneous events, starting from the formation of alcohol:MnO₄⁻ complex, multiple-electron transfer between the species with possible formation of aqueous intermediates of manganese ranging from Mn(VI) to Mn(III),^{31,36,43,73} disproportionation (for Mn species other than Mn(IV)) and hydrolysis of these species and finally their condensation into a 3D network of [-Mn-O-Mn-] chains – forming MnO₂.⁷⁴ All these reactions are additionally affected by phenomena specific to aqueous phase, for example, the formation of a double layer and charging of solid surfaces (resulting in e.g. coulombic repulsion between solid MnO₂ and MnO₄⁻)⁵⁰ or pH-dependent equilibria of multiple ions involved in each step of the reaction. The dynamics of all these nearly simultaneous processes, together with entrapment of water⁷⁵ and ionic species⁴⁸ (such as K⁺), result in more disordered arrangement of Mn-O moieties and lower compactness and macro-crystallinity of the layer.

Besides of improving MnO₂ crystallinity, the higher temperature during the KMnO₄ sub-cycle could accelerate the overall RLD deposition, since the increase of temperature by as little as 10 °C was shown to double the rate of PA reaction with KMnO₄.³¹ The effect of temperature on the PA sub-cycle can be more complex. From the thermodynamic point of view, studies of inhibition efficiency of PA during corrosion of metals in H₂SO₄ and NaOH indicated that the equilibrium amount of adsorbed PA decreases with increasing temperature, which can be due to increased PA desorption and substitution with re-adsorbing water molecules.^{76,77} In our case, however, this effect could be negligible due to the large excess of PA molecules in the 0.1 M solution. It is worth noting that the corrosion inhibition studies of iron in HCl showed an actual increase in PA adsorption with temperature due to the formation of polymeric PA films at higher temperature^{27,78} (polymerization of PA was also reported in the pure aqueous solution heated at 95 °C).²² From the kinetic point of view, although the increase of temperature decreases the time needed to reach the adsorption equilibrium, it may also accelerate the side reaction of PA with the as-deposited MnO₂,⁴⁶ which

could decrease the saturation GPC and increase porosity of the end material. Therefore, the effect of temperature on the growth of the layer remains open for further investigations.

The growth of MnO₂ on wafers coated with different metals and metal oxides was analyzed using the immersion times of 1 min (PA) / 1 min (KMnO₄) (Figure 5d); i.e. at the saturation for Ni substrates. We found a positive growth of MnO₂ on Ni, Ti, Pt and TiO₂, but no growth was observed on Al₂O₃ and SiO₂ (although deposition of a visibly non-uniform coating was possible on silica by minimizing the rinsing time with H₂O between consecutive steps). While the numerical differences between the observed growth rates can be related to the non-equal roughness of the analyzed substrates (Figure S7), the qualitative differences in the MnO₂ growth must originate from the particular chemical phenomena occurring at the analyzed surfaces. First, the initiation of the growth is easier on oxidizable substrates (such as metals) due to the reaction of MnO₄⁻ with the substrate surface during the first RLD cycle, as described by Equations 7a-b for a Ni surface (note that the top TiO₂ surface also contains a certain amount of oxidizable Ti³⁺).^{79–81} The reaction with the substrate also helps to form strong bonding of the MnO₂ seeds to the substrate, increasing the adhesion of the deposited layer. The quantity of MnO₂ formed in this reaction depends both on the stoichiometry of metal oxidation reaction and on the attainable thickness of the surface metal oxide/hydroxide. For example, titanium tends to form thicker surface oxides than nickel, which can partially explain the higher initial amount of MnO₂ on Ti than on Ni.^{82–84} However, the initial amount of MnO₂ should be also larger on Ni than on Pt (limiting surface PtO thickness of ~1 monolayer)⁸⁵ which is not evident in our case. The second reason for the observed differences can be thus related to the different strength of adsorption of propargyl alcohol on the analyzed substrates. Our results indicate that the Lewis acidity of the surfaces has no apparent influence on the growth – in the 0.1 M PA solution with pH = 6.95, SiO₂ surface is basic and Al₂O₃ acidic,⁴⁹ and both exhibit no GPC. However, the qualitative differences between GPC seem to be in general agreement with the differences in surface free energies (γ) of the pure substrates: $\gamma_{\text{Pt}} \approx \gamma_{\text{Ni}} \approx \gamma_{\text{Ti}} > \gamma_{\text{TiO}_2} \approx \gamma_{\text{Al}_2\text{O}_3} > \gamma_{\text{SiO}_2}$ (Table S1, note, however, that the true surface energies can differ due to the presence of native oxides or chemisorbed organic contaminants). It is also natural that the high energy surfaces show high tendency to adsorb species (e.g. PA) in order to lower the overall energy of the system. Since a high surface energy in principle results in intrinsic hydrophilicity of a clean surface (not accounting for the roughness effects), and PA molecules have a similar dipole moment to water,²² we can also expect that the intrinsically hydrophilic surfaces will show higher affinity to PA than intrinsically hydrophobic surfaces. Nevertheless, all the analyzed substrates were hydrophilic after cleaning, yet not all allowed for detectable growth of MnO₂, which points to the importance of specific electronic effects between the surfaces and the adsorbates at the atomic scale.

Microscopically, the PA adsorption – and thus the MnO₂ growth – could be promoted by the presence of accessible d-orbital electrons at the substrate's metal atoms or ions (again, although Ti⁴⁺ in bulk TiO₂ has no d-orbital electrons, the oxygen vacancies common to the surfaces of TiO₂ result in partial filling of surface d-orbitals).^{79–81} This observation is in agreement with the studies of adsorption of alkynes on transition metals and of acetylenic alcohols on iron, which was previously described to occur by back-donation of the substrate d-orbital electrons to the π^* -antibonding orbitals of the acetylenic molecule.^{30,86–88} Other studies also showed that the stabilizing energy of adsorption of PA on platinum can be more than twice than that on aluminum.^{89,90} In our case, such interactions can also promote adsorption of PA to the MnO₂ formed in the previous deposition cycles, facilitating continuous growth of the layer. Nevertheless, one could expect that the growth rate becomes independent of the substrate chemistry once a thin MnO₂ layer is formed, which is not apparent from our results, at least in the studied range of deposition cycles. Bearing in mind the non-equal roughness of the analyzed substrates, the differences in the growth rates could also be inherited from the different nature of MnO₂ seed layer formed on the substrates with various electronic configuration. Therefore, while these results show that the RLD can be performed on a broader range of substrates, a more detailed study is needed to verify the exact mechanism responsible for the growth on various surfaces.

To validate the applicability of our method for coating high aspect ratio surfaces, we applied it onto a sample of interconnected nickel nanowire mesh (Figure 6a). This material, recently developed in our group, consists of a 3D network of densely packed nickel nanowires (pore size of 64 ± 17

Figure 6. Coating the nanomesh with MnO_2 . (a) SEM image of the nanomesh network, (b) Bright Field TEM images of the nanowires scratched from the wafer after 15 RLD cycles, (c) Annular Bright Field (ABF) and Dark Field (ADF) STEM images of a nanowire after coating, together with corresponding EDX elemental mapping for Ni (purple) and Mn (yellow), (d) High Angle Annular Dark Field (HAADF) STEM image and corresponding EDX elemental maps of the nanomesh cluster for Ni (purple), Mn (yellow) and O (red), (e) EDX-SEM quantification of Mn content along the depth of the nanomesh, after 15 RLD cycles (left) and 140 thermal ALD cycles (right).

nm) and is a representative nanostructured current collector for e.g. 3D microbatteries.⁹¹ The $\sim 3.5 \mu\text{m}$ thick nanomesh used in this work is supported on a TiN/Ti/Si wafer, exhibits a thickness-to-pore size ratio of $\times 55$ and a total surface area of 235 cm^2 per sample. For a comparison, we subjected the same type of sample to a thermal ALD of MnO_2 , using $\text{Mn}(\text{thd})_3$ and ozone precursors. In both the RLD and thermal ALD, the number of cycles was adjusted to deposit $\sim 2 \text{ nm}$ of MnO_2 , using deposition conditions previously optimized for the planar Ni samples.

The nanomesh after 15 RLD cycles was characterized with TEM. The bright field images show a distinguishable layer coating the surface of the nanowires (Figure 6b). While such layer could be due to a passive nickel oxide/hydroxide, the EDX-STEM elemental maps indicate that the coating corresponds to MnO_2 (Figure 6c). The layer thickness derived from the STEM images equaled $3 \text{ nm} \pm 1 \text{ nm}$, which is not far from the expected thickness of 2.1 nm after 15 cycles (Figure 5b). The elemental maps in Figure 6d show that MnO_2 covers conformally the walls of even the most complex mesopores of the nanomesh. Notably, the coating resisted 10 minutes of ultrasonication in acetone, which was applied to disperse the nanowires prior to their loading onto a TEM grid.

We also analyzed the distribution of the manganese oxide along the depth of the nanowire network, by quantifying Mn / Ni ratio with EDX-SEM (Figure 6e). Redox layer deposition resulted in an even distribution of the coating within the entire thickness of the nanomesh (standard deviation = 8%, partially due to X-ray scattering on the nanowires). In contrast to the RLD, thermal ALD resulted in deposition of manganese oxide only at the top part of the nanomesh, as evidenced by the rapid decay of Mn along the depth of the nanowire network. While in theory thermal ALD should give an ideal conformality due to much faster diffusion of gases in vacuum, the observed non-uniform distribution of the MnO_2 coating is likely related to the catalytic decomposition of ozone on the surface of as-formed MnO_2 , which has been previously recognized by Nielsen as a challenge for the uniform ALD of this particular manganese oxide.¹⁵ Contrary to the ALD of MnO_2 on planar substrates, the high surface area of MnO_2 on the nanowires increases its activity towards decomposing O_3 into oxygen, depleting the active gas before it can reach the interior of the nanomesh. Since the presence of ozone (rather than oxygen) is essential for the uniform formation of MnO_2 during oxidation of adsorbed $\text{Mn}(\text{thd})_2$ in the second ALD sub-cycle,^{15,17} the parasitic decomposition of O_3 inside the nanomesh minimizes deposition of MnO_2 in the bulk of the nanowire network.

Figure 7. (a) XRD spectra of the pristine and processed samples, (b) Cyclic voltammograms of the RLD- and ALD-coated samples in $1 \text{ M LiClO}_4/\text{propylene carbonate}$, recorded at 5 mV/s . The asterisks (*) in (a) annotate the peaks of the wafer substrate (TiN, Ti and Al).

After the coating, the nanowires retained their metallic state, as verified with grazing-incidence X-ray diffraction (XRD) (Figure 7a). Compared to the pristine nanomesh sample, the diffractograms of the samples processed with RLD and thermal ALD show only a small increase of the NiO signal at 37.2° and 62.9°. Lack of oxidation of nickel is important for the electrochemical applications (e.g. supercapacitors or batteries), where oxidation of a current collector would result in failure of the electrode. The diffractogram of the nanomesh sample after RLD also exhibits a small, broad peak at about 18.5°, which can correspond to nanosized (111) planes of cubic λ -MnO₂ (JCPDS card #42-1169) or (200) planes of tetragonal α -MnO₂ (JCPDS card #44-0141).

Finally, we tested the samples for their electrochemical activity by performing cyclic voltammetry (CV) in 1 M LiClO₄ / propylene carbonate (Figure 7b). The response of the sample processed with thermal ALD is mostly due to the capacitive charging of nickel nanomesh – as indicated by the lack of clear redox peaks and the symmetric hysteresis of the current in the entire potential range. A trace cathodic peak can be observed at 2.65 V vs. Li⁺/Li, corresponding to lithium insertion into the minute quantity of MnO₂. The ALD MnO₂ was demonstrated in earlier work to show clear redox peaks upon lithiation,¹⁷ further indicating that the absence of these peaks here corresponds to the absence of a film. Contrary to that, the sample coated using RLD exhibits significantly higher currents and visible cathodic and anodic shoulders at 2.65 V and 3.6 V vs. Li⁺/Li, corresponding to the reversible lithium intercalation in MnO₂:

The large width and separation of the redox peaks is, however, different from the sharp peaks observed by Mattelaer *et al.* on planar ALD-grown MnO₂.¹⁷ The broadening of the peaks is related to the hydrous and generally amorphous nature of the as-deposited MnO₂, which typically requires annealing at higher temperatures to remove the structural water and facilitate Li⁺ intercalation.^{92,93} Nevertheless, the RLD allowed coating the entire surface of the nanostructured current collector with MnO₂, resulting in a significantly higher electrochemical activity of the electrode, which is promising for its future electrochemical applications.

DISCUSSION AND CONCLUSIONS

In this work, we have developed a method for coating planar and high aspect ratio substrates with MnO₂ of controllable, nanometer-scale thickness. The method is based on a cyclic reduction of aqueous KMnO₄ with monolayers of propargyl alcohol adsorbed on the substrate surface. Consequently, the amount of deposited manganese oxide can be controlled with the number of deposition cycles with close-to-a-monolayer precision. Also, thanks to the self-limiting adsorption of the alcohol, the growth in each cycle shows an ALD-like saturation behavior. Because of the high adsorption density of the small precursor molecules and ions, the observed growth per cycle is about 5x higher and 1.5x faster than that of thermal- and plasma-enhanced ALD. The processing is done in air and at room temperature, using aqueous solutions of common chemicals and simple glassware, which makes it accessible to virtually any laboratory. The simplicity of the method also reduces its processing costs, eliminating the need for expensive, custom made thermal vacuum equipment and moisture-sensitive precursors, which is a clear advantage towards potential upscaling of the deposition. The method also enabled coating of MnO₂ onto a high aspect ratio Ni nanowire mesh, which was unsuccessful with thermal ALD due to ozone decomposition. This does not entirely rule out the possibility of ALD of MnO₂ on such high aspect ratio substrates, which may be enabled by e.g. increasing ozone dosing,¹⁵ or by electrooxidation of ALD-deposited MnO (the ALD of which utilizes water vapor instead of ozone),⁹⁴ although with clearly higher complexity. Compared to RLD, thermal ALD of MnO₂ remains advantageous for coating planar or low-aspect-ratio substrates in terms of crystallinity, density and purity of the deposited layer (although the level of potassium impurities in the RLD-MnO₂ can be potentially decreased by adjusting the pH during the deposition). Also, the hydrous and amorphous nature of MnO₂ grown with RLD at room temperature results in intrinsically poorer electrochemical properties compared to the anhydrous and more crystalline MnO₂ prepared with thermal ALD.¹⁷ This issue can be potentially alleviated by post-annealing of the RLD layer at or below 350 °C, which can remove structural defects, improve crystallinity and eliminate water from the MnO₂ – improving its performance as a Li-ion electrode.⁹³ Also, currently the RLD method allows deposition on substrates

made of transition metals and their oxides, while the typical ALD is compatible with a broader range of substrates, such as Si, SiO₂ or Al₂O₃.^{15,17} However, we believe that our approach could also be extended to such substrates, provided that an appropriate organic precursor is chosen. Such precursor should exhibit strong adsorption on the substrate surface and possess functional groups able to reduce MnO₄⁻, such as -OH, -C=C- or -CHO. Complementarily to ALD, the redox layer deposition is an attractive method for coating thin layers of manganese dioxide onto high aspect ratio structures, which is promising for its numerous (electro)chemical applications.

EXPERIMENTAL SECTION

Chemicals. Propargyl alcohol (99%, Sigma Aldrich) was used as received to prepare the 0.1 M solution. To prepare the 0.1 M solution of potassium permanganate, the KMnO₄ powder (≥99.0%, Sigma Aldrich) was weighed on an analytical balance and dissolved in a 1 L volumetric flask. Then it was then boiled in a 5 L glass beaker for 1 hour, cooled down to the room temperature, stored in dark for 5 days and filtered into a dark-glass storage flask to remove any trace MnO₂. Na₂SO₄ (≥99.0%, Sigma Aldrich) was used as received.

RLD of MnO₂. The typical deposition was performed on 150 nm PVD-sputtered Ni, stacked on 150 nm TiN/Si wafers. Prior to the deposition, the sample coupons (2.4 x 12 cm) were cleaned by ultrasonication for 10 min in acetone and for 10 min in isopropanol, followed by drying in nitrogen stream. The deposition was carried out by cyclic immersion of the coupon in two piranha-cleaned 50 mL glass cylinders filled with 0.1 M propargyl alcohol and 0.1 M KMnO₄ (see Figure S1 for the photograph of the setup). Between each immersion, the wafer coupon was rinsed under a steady stream of high purity water for 5 s each time. The walls of the cylinder containing KMnO₄ were covered with an Al-coated scotch tape to prevent light-induced precipitation of MnO₂. During the processing, the wafer coupon was held by a clean Au-coated metallic clamp. After each given number of RLD cycles (5, 10, 15, 20, 25, 30 and 35), the bottom 2 cm part of the wet wafer coupon was cut off using clean pliers, washed with water, dried with nitrogen gun and stored for characterization. The remaining part of the wet wafer coupon was washed with water and the processing was continued, repeating the cutting procedure every 5 cycles. All the handling of the samples was done using clean ceramic tweezers. The deposition was done inside a fumehood to avoid exposure to the harmful vapors of propargyl alcohol.

The deposition on interconnected nanowires (nanomeshes) was performed on 2.5 cm² circular nanomesh samples fabricated on 2.4 x 2.4 cm coupons of Al/TiN/Si wafers according to the previously reported procedure.⁹¹ The deposition was carried out using 1 min immersion times for both PA and KMnO₄.

Thermal ALD of MnO₂. Thermal ALD of MnO₂ was performed on the same type of nanomesh sample. The ALD was carried out in a high-vacuum chamber (base pressure 10⁻⁷ mbar), using Mn(thd)₃ (Strem, 99%) and ozone (>150 µg/mL, produced from pure O₂ with an OzoneLab generator), similarly to the previously described procedure.¹⁷ Briefly, each ALD cycle consisted of 3 subcycles of static pulsing of Mn(thd)₃/Ar at 1 mbar for 10 s and evacuation to 10⁻⁶ mbar, followed by 3 subcycles of static pulsing of O₃ at 1 mbar for 10 s and evacuation to 10⁻⁶ mbar. The Mn(thd)₃ precursor bottle was maintained at 133°C, the gas line at 135°C, reactor walls at 140°C and the sample at 180°C.

Characterization. Scanning electron microscopy (SEM) was performed using FEI Nova SEM coupled with INCA PentaFETx3 Energy dispersive x-ray (EDX) spectrometer from Oxford Instruments. Transmission electron microscopy (TEM, HAADF-STEM and EDS maps) was performed using FEI Titan G2 60-300 equipped with Super-XTM X-ray detectors system.

X-ray photoelectron spectroscopy (XPS) spectra were recorded by a Thermo Scientific K-alpha+ system using monochromatic Al Kα X-rays. The spot size of the beam was 400 µm and the base pressure of the system was 10⁻⁸ mbar. The spectra were calibrated against carbon reference at 284.8 eV.

Energy dispersive X-ray fluorescence spectroscopy (XRF) was performed with Mavorn/Panalytical Epsilon 5 equipped with Ge detector. Manganese Kα1 line was used for quantification of manganese content on surfaces of the samples. To cross-calibrate the XRF signal, Rutherford backscattering spectrometry (RBS) was used. Seven Ti/Si wafer coupons coated after 5-35

RLD cycles were measured with RBS, and, independently, with XRF. The average XRF absorbance / RBS Mn atom concentration ratio was used as a reference for all the XRF measurements. The RBS experiment was conducted with an He⁺ beam with an energy of 1.523 MeV. The D1 scattering angle was set at 170° and the sample tilt angle at 11°, the current on sample was 31 nA. For the analysis, the IMEC in-house developed software *SA-numeric integration/Arriba* was used.

Grazing incidence X-ray diffraction (XRD) was performed using PANalytical X'Pert MRD diffractometer equipped with Cu K α radiation (λ =1.540598 Å), at the incidence angle Ω of 1° in the 2θ range of 10–70° with the step size of 0.020° and the step time of 12.25 s/step.

Cyclic voltammetry (CV) in aqueous Na₂SO₄ was performed using Autolab PGSTAT100 potentiostat/galvanostat, in a 3-electrode setup, using AgCl/Ag/3M KCl reference electrode and a platinum mesh counter electrode. CV testing for Li⁺ insertion was performed inside an Ar-filled glove-box (O₂, H₂O < 10 ppm), using Autolab PGSTAT 301 potentiostat/galvanostat. The measurements were done using a dedicated teflon cell, in a 3-electrode setup, where the sample was connected as a working electrode and two stripes of lithium ribbon (99.9%, Sigma Aldrich) were used as counter and reference electrodes. Prior to the measurements, the samples were dried overnight at 120°C in air. The measurements were recorded in 1 M LiClO₄ / propylene carbonate, at the scanning speed of 5 mV/s.

ASSOCIATED CONTENT

Supporting Information. Equations of oxidation reactions of propargyl and allyl alcohol; calculations of free Gibbs enthalpy of surface oxidation, table showing surface free energies of various solids, photograph of an RLD setup; linear scan voltammogram of the sample after 15 RLD cycles in KOH; SEM image of the top surface of Ni wafer after 35 RLD cycles; EDS-STEM spectra of the deposited MnO₂; cyclic voltammograms of the samples processed with increasing number of RLD cycles; SEM images of some of the substrates analyzed for the growth of MnO₂. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

S.P.Z. conceived the idea and performed the depositions together with L.H., who also assisted in data analysis. F.M. performed thermal ALD of MnO₂ in the laboratory of C.D. M.R. performed XRF characterization and O.R. performed TEM-EDS analysis. P.M.V. supervised the project and assisted in design of experiments and data interpretation. The manuscript was written by S.P.Z. and revised by P.M.V., F.M. and C.D., with the valuable input from all authors. All authors have given approval to the final version of the manuscript.

Notes

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ABBREVIATIONS

RLD, redox layer deposition, PA, propargyl alcohol, GPC, growth per cycle, XRF, X-ray fluorescence spectroscopy, RBS, Rutherford backscattering spectrometry.

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