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The role of electronic and ionic conductivities in the rate performance of tunnel structured manganese oxides in Li-ion batteries

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Single nanowires of two manganese oxide polymorphs (α-MnO₂ and todorokite manganese oxide), which display a controlled size variation in terms of their square structural tunnels, were isolated onto nanofabricated platforms using dielectrophoresis. This platform allowed for the measurement of the electronic conductivity of these manganese oxides, which was found to be higher in α-MnO₂ as compared to that of the todorokite phase by a factor of ~46. Despite this observation of substantially higher electronic conductivity in α-MnO₂, the todorokite manganese oxide exhibited better electrochemical rate performance as a Li-ion battery cathode. The relationship between this electrochemical performance, the electronic conductivities of the manganese oxides, and their reported ionic conductivities is discussed for the first time, clearly revealing that the rate performance of these materials is limited by their Li⁺ diffusivity, and not by their electronic conductivity. This result reveals important new insights relevant for improving the power density of manganese oxides, which have shown promise as a low-cost, abundant, and safe alternative for next-generation cathode materials. Furthermore, the presented experimental approach is suitable for assessing a broader family of one-dimensional electrode active materials (in terms of their electronic and ionic conductivities) for both Li-ion batteries and for electrochemical systems utilizing charge-carrying ions beyond Li⁺. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). [http://dx.doi.org/10.1063/1.4948272]

With society moving away from burning fuels for electricity production and towards more sustainable energy sources, Li-ion batteries have become an appealing option for powering electric vehicles, providing grid level storage for alternative energy sources, and powering mobile electronics. As a result, there has been much research directed at developing and improving Li-ion battery systems, with a large number of chemistries having been explored over the years. Advances in the field of Li-ion batteries have resulted in the identification of a number of important properties for materials to be considered viable candidates for electrodes in Li-ion batteries. Amongst other factors such as material cost, toxicity, and chemical stability, it is well known that battery electrode materials must be good electronic and ionic conductors in order to demonstrate high performance. These parameters are not only important in Li-ion batteries, but also in intercalation based energy storage systems operating due to the reversible intercalation of ions other than Li⁺, such as in Na-ion batteries and beyond.

Electronic and ionic conductivity each play a significant role during the intercalation/deintercalation of charge-carrying ions within an electrode material. The efficient movement of electrons...
and ions becomes especially important at high current rates when a large amount of charge must be utilized in a short amount of time. Many common battery applications often demand these high amounts of power, such as electric vehicles when fast acceleration is needed or grid-level storage when quick load leveling is required. However, at high charge/discharge rates, it has been found that there is a substantial decrease in battery performance, with the capacity of the battery material often dropping significantly.3,7,8 This has been attributed to Li+ ions and/or electrons not being able to move through the material quickly enough to utilize all stored chemical energy. If Li-ion batteries are to become viable candidates for widespread use in high power applications, this is an imperative factor to be improved.3,7

Past work, such as on the highly studied LiFePO4 cathode material, has indicated that low electronic conductivity is detrimental to performance at high current rates.9 The electronic conductivity of LiFePO4 is extremely low (~10^{-9} S/cm),10 resulting in only partial Li+ ion insertion/extraction and unattractively low capacity values at high rates. However, when nanostucturing of LiFePO4 particles to reduce charge carrier transport lengths was combined with the application of a uniform coating of carbon to improve the material’s electronic conductivity, the electrochemical capacity of LiFePO4 was significantly increased.9 Although there was a great deal of focus on electronic conductivity for LiFePO4, it is fundamentally understood that both the electronic and ionic conductivities are important in the performance of mixed conducting electrodes at higher current rates, and this has been reinforced in more recent works.7,8,10 Nonetheless, the exact relationship between these two parameters and their effect on electrochemical performance, especially at high current densities, is still uncertain throughout many materials systems. Further, as evidenced by the performance of LiFePO4, the electronic conductivity of a material can play a different role in different electrode materials systems.

Measurement of the ionic conductivity of a material can be performed via a number of well-established electrochemical methods including electrochemical impedance spectroscopy (EIS) and galvanostatic intermittent titration technique (GITT).7 Although these techniques are performed on battery electrodes composed of active material, a conducting agent, and a polymer binder, the measured ionic conductivity can be considered to be intrinsic to the active material of the battery electrode since only the active material participates in the conduction of charge-carrying ions. For Li-ion batteries, the ionic conductivity of electrode materials is often expressed in terms of the Li+ ion diffusion coefficient (D_{Li^+}), which is a representation of how far a given Li+ ion can travel in a given amount of time.

The measurement of the electronic conductivity of a material can also be performed via different methods. Traditionally, the electronic conductivity of an electrode film containing the active material of interest, conductive additives (e.g., carbon), and a polymer binder is measured using a four point probe method.7,11 This method measures the electronic conductivity of an entire electrode film, which includes the effects of the film additives, as well as the intergrain boundaries within the film, resulting in an electronic conductivity value that may differ significantly from that which is intrinsic to the active material itself. This effect can be further increased by the fact that, due to common experimental setups, there is variability and difficulty in maintaining proper contact with electrode films without introducing damage because pressure is neither controllable nor known.11 Even in commercial electrode film preparation methods, there is variability in film composition that may affect electronic conductivity measurements.12 Therefore, in order to accurately obtain the electronic conductivity, which is intrinsic to an active electrode material (as per the definition of the term “electronic conductivity” for a given material), these effects must be eliminated. We accomplish this by utilizing a platform that allows for the isolation of a single nanostructure via dielectrophoresis (DEP) (Figure 1).13-18 The electronic conductivity of the assembled nanostructured material is extracted using a method that employs two-terminal current vs. voltage (I-V) measurements on multiple samples with different geometries.15,19 This approach allows for the measurement of the electronic conductivity, which is intrinsic to these two tunnel manganese oxides polymorphs, for the first time. These measurements are made on a scale similar to that in which charge-carrying ions diffuse through, providing useful information for analyzing electrochemically active materials.

In this work, we investigate the effect of measured electronic and reported ionic conductivities on the rate performance of manganese oxides with intercalation favorable tunnel crystal structures
in Li-ion batteries. Although in this paper we focus on tunnel manganese oxides, ionic and electronic conductivities have been investigated for other electrochemically active materials systems as well.\textsuperscript{20–22} Manganese oxides are of great interest in Li-ion battery applications because of their low cost, low toxicity, and high electrochemical activity.\textsuperscript{23–26} We focused this study on investigating two tunnel manganese oxide phases with nanowire morphologies, $\alpha$-MnO$_2$ and todorokite manganese oxide, and we compare the rate performance of these two polymorphs in Li-ion batteries for the first time. By relating this electrochemical performance to the intrinsic electronic conductivities measured on single nanowires with the DEP-assisted platform and the Li-ion diffusion coefficient values reported in the literature for $\alpha$-MnO$_2$ and todorokite manganese oxide, we develop a correlation between these factors and elucidate the importance of each conductivity parameter in the higher rate performance of tunnel-structured manganese oxides in Li-ion batteries.

$\alpha$-MnO$_2$ and todorokite nanowires were synthesized via a hydrothermal method. For $\alpha$-MnO$_2$, the method is described elsewhere.\textsuperscript{27} Briefly, 2 mmols each of KMnO$_4$ (Acros Organics, 99+% and NH$_4$Cl (Strem Chemicals, 99.5%) was mixed in 100 ml of deionized water, and 20 ml of this solution was placed in 23 ml Teflon-lined stainless steel autoclaves (Parr Instrument Company). The autoclaves were placed in an oven for 48 h at 150 °C, followed by filtering, washing, and drying of the products at 100 °C for 12 h under vacuum. The todorokite manganese oxide nanowires were synthesized following a previous report.\textsuperscript{28} In short, a solution consisting of 50 ml of 1M NaOH (Acros Organics, 99+% and 50 ml of 2M H$_2$O$_2$ (Fisher Scientific, 30 wt. %) was added while stirring to a 50 ml solution of 0.3M Mn(NO$_3$)$_2$ (Alfa Aesar, 99.9%). After allowing reaction to proceed for 30 min, the product (Na-birnessite) was filtered and washed. In order to create Mg-buserite from the Na-birnessite, Mg$^{2+}$ was exchanged with Na$^+$ via 72 h of stirring the Na-birnessite in 1M MgCl$_2$ (Acros Organics, 99+% solution). The solution was replaced every 24 h and after the ion-exchange treatment was completed, the final Mg-buserite product was filtered, washed, and dried at 100 °C for 12 h under vacuum. 100 mg of the dried Mg-buserite was dispersed in 17 ml of 1M MgCl$_2$ solution, and this mixture was added to a 23 ml Teflon-lined stainless steel autoclave that was subsequently placed in an oven for 96 h at 220 °C. The resulting todorokite nanowire product was filtered, washed, and dried at 100 °C for 12 h under vacuum.

Scanning electron microscope (SEM) images of the nanowires in powder form (i.e., bulk-scale) were obtained using a Zeiss Supra 50VP (Germany) microscope equipped with an energy dispersive X-ray spectroscopy (EDS) attachment for evaluating the chemical composition of the manganese oxides. EDS spectra were recorded in multiple 10 $\mu$m by 10 $\mu$m areas to ensure repeatability of results, and all spectra were averaged to determine composition of materials. Crystal structure and phase information were investigated via powder X-ray diffraction using a Rigaku SmartLab powder diffractometer (Japan) with Cu Kα radiation in a Bragg-Brentano configuration with a step size 0.02°.

Single nanowires of $\alpha$-MnO$_2$ and todorokite phases were integrated onto nanofabricated silicon chips using dielectrophoresis (DEP), as described in our past reports.\textsuperscript{13–15} The assembly platform
consisted of silicon chips with an insulating layer of 100 nm thick nitride film on the top-side to provide device isolation. Gold nanoelectrode pairs were fabricated on these substrates using the thin film lift-off of gold within electron beam lithography defined resist patterns. These gold nanoelectrode pairs were separated by design gaps that varied between 200 nm and 800 nm in different designs. This inter-electrode separation is used to vary the length of the assembled nanowire devices, which is then exploited to extract the electronic conductivity of the nanowires through these geometry-induced variations in intrinsic resistance of the assembled devices. Single nanowires were assembled across these gold electrodes using DEP through a suitable control of deposition parameters such as AC field strength, frequency, capture time, and electrode geometry. In this technique, a non-uniform electric field is exerted in the vicinity of the electrodes using an AC excitation field and the nanowires are captured on to the gold electrodes from their respective fluidic suspensions (in ethanol) through the interactions of their respective, induced dipole with this AC field excitation. After nanowire capture, the chip is dried with a nitrogen gun to remove the fluidic suspension. Next, platinum (Pt) metal is deposited on top of the assembled nanowires using the electron beam induced deposition (EBID) technique inside a Zeiss Auriga FIB-SEM system. This top-side metallization improves the electrical contact to the nanowires through a reduction in the contact resistance at the electrode-nanowire interface. SEM and tapping-mode AFM images of the nanowires are then used to extract the length and diameter of the nanowires, respectively. SEM images of the single nanowire devices were acquired using the secondary electron detector of a Hitachi SU-70 microscope at an acceleration voltage of 2 kV. The length of the nanowires from these micrographs was extracted using the ImageJ software. Atomic force microscopy was performed using a VEECO Icon AFM in the tapping mode. The imaging was performed using SiN tips with a spring constant of ~0.6 N/m. The nanowire diameter was acquired from height plots of the device, which were taken along a direction that is orthogonal to the longitudinal axis of the nanowire.

Electrical transport measurements are performed on the single nanowire samples using a Keithley 2636B sourcemeter. In this experiment, the voltage across the distal contacts is swept from 0 to a few volts (1 V for α-MnO$_2$ and 3 V for todorokite manganese oxide), and the device currents are recorded during this process. The resulting I-V plots are used to extract the two-terminal resistance of the single nanowire devices. Next, the variations in nanowire diameter (arising from the geometric distribution observed in the synthesized samples) and nanowire device length (arising from intentional variations in device design and from the orientation of the assembled nanowires with respect to the electrode gaps) are leveraged to extract the nanowire electronic conductivity and contact resistance from the measured two-terminal resistance.

For electrochemical characterization, electrode films consisting of 70% active material, 20% acetylene black (Alfa Aesar, 99.9%), and 10% poly(vinylidene fluoride) binder (Alfa Aesar) dispersed in 1-methyl-2-pyrrolidone (Alfa Aesar, 99.5%) were cast using a doctor blade onto an aluminum foil current collector. After the cast electrode films were allowed to dry, 12 mm disc electrodes were punched and dehydrated at 100 °C for 12 h under vacuum before transfer into an Ar-filled glovebox. Active material loading of the electrodes was approximately 0.44 mg/cm². Type 2032 coin cells were used to electrochemically test the electrodes in a Li-ion battery half-cell configuration, and assembly of the cells was performed in the glovebox box’s inert atmosphere to minimize exposure to water and oxygen contamination. The Li-ion coin cells were assembled with lithium metal (Alfa Aesar, 99.9%) as the counter and reference electrodes, a polypropylene membrane (Celgard) as the separator, and 1M LiPF$_6$ (Alfa Aesar, 99+% in a 1:1 mixture of ethylene carbonate (Acros Organics, 99+% and diethyl carbonate (Acros Organics, 99+%) as the electrolyte solution. Galvanostatic cycling of the assembled coin cells was performed using a battery testing station (Arbin Instruments, USA). Cycling was performed at various current rates in a voltage range of 1.5-4.0 V vs. Li/Li$^+$ for α-MnO$_2$ and 2.0-4.2 V vs. Li/Li$^+$ for todorokite manganese oxide.

Figures 2(a) and 2(b) show the crystal structure schematics for α-MnO$_2$ and todorokite manganese oxides. The two materials are built by corner and edge sharing MnO$_6$ octahedra building blocks forming similar square tunnel configurations. α-MnO$_2$ (Fig. 2(a)) possesses the two octahedra by two octahedra structural tunnels with a side length of 4.6 Å, and todorokite (Fig. 2(b)) possesses the three MnO$_6$ octahedra by three MnO$_6$ octahedra structural tunnels having a side length of 6.9 Å. These materials are both stabilized by cations, with α-MnO$_2$ containing K$^+$ ions within its tunnels.
FIG. 2. Crystal structure schematics for (a) α-MnO$_2$ (K$_{0.11}$MnO$_2$) and (b) todorokite MnO$_2$ (Mg$_{0.20}$MnO$_2$). (c) and (d) show representative XRD patterns for α-MnO$_2$ and todorokite, respectively.

and todorokite containing Mg$^{2+}$ ions. The stabilizing K$^+$ and Mg$^{2+}$ ions only partially occupy the space inside structural tunnels, leaving enough volume for Li$^+$ ion intercalation (see Figure S1 of the supplementary material for schematic representation of α-MnO$_2$ and todorokite crystal structures in relation to Li$^+$ ion size$^{30}$). Further, as a result of the difference in size of the crystal tunnels, and in the size/charge of the stabilizing cations, it can be expected that Li$^+$ ions diffuse through the two materials at different rates. In fact, the reported D$_{Li^+}$ values for the manganese oxides investigated in this work are separated by several orders of magnitude. For α-MnO$_2$ stabilized by K$^+$ ions, past works have reported D$_{Li^+}$ values ranging from $1 \times 10^{-12}$ cm$^2$/s for the fully charge state (no lithium inserted) to $2 \times 10^{-11}$ cm$^2$/s for the fully discharged (lithiated) state.$^{31-33}$ For todorokite manganese oxide, D$_{Li^+}$ values of approximately $1 \times 10^{-7}$ cm$^2$/s for the fully charged state and $2 \times 10^{-10}$ cm$^2$/s for the fully discharged state have been reported.$^{34}$ Thus, the reported D$_{Li^+}$ values are greater for todorokite than α-MnO$_2$, and it is believed to be a result of both the larger tunnel size and smaller stabilizing cation size (ionic radius of 138 pm for K$^+$ and 72 pm for Mg$^{2+}$)$^{35}$ for todorokite.

Formation of α-MnO$_2$ and todorokite phases was confirmed by XRD analysis (Figures 2(c) and 2(d)). Both XRD patterns are in good agreement with past reports for these materials.$^{27,36}$ For α-MnO$_2$, all peaks can be indexed to a tetragonal phase with I4/m symmetry (JCPDS #44-0141), and for todorokite, the pattern being readily indexed to the monoclinic P2$\bar{1}$m tunnel structured phase (JCPDS #38-475). No impurity phases are detected in either XRD patterns.

SEM images of α-MnO$_2$ and todorokite nanowires are shown in Figures 3(a) and 3(b). It can be clearly seen that both materials are completely composed of high aspect ratio, flexible, and uniform one-dimensional crystals. Both types of nanowires are similar in dimension, with various diameters up to 100 nm and lengths of several microns. Some of the nanowires are agglomerated along their long axis, forming thicker bunches. This is a result of the wires growing coaxially as bundles, and it has been demonstrated that these bundles can be broken by sonication.$^{15}$ Past works for nanowires of these materials have shown that the tunnel structures grow parallel to the nanowires’ long axis,$^{27,28}$ creating well-defined, one-dimensional diffusion pathways for charge-carrying ions along the nanostructures. EDS analysis of the nanowire composition confirmed the presence of stabilizing cations in the manganese oxide structures (Figures 3(c) and 3(d)). From EDS, the average
FIG. 3. SEM images [(a) and (b)] and representative EDS spectra [(c) and (d)] for $\alpha$-MnO$_2$ and todorokite nanowires, respectively. (e) and (f) show AFM images of individual nanowires of $\alpha$-MnO$_2$ and todorokite, respectively. These images show the assembled nanowires with their top-side Pt clamping at the distal ends in order to improve the electrical contact to the nanowires. The insets to these images show the SEM image acquired before the deposition of Pt. (g) and (h) show the tapping mode AFM-based height plots of the $\alpha$-MnO$_2$ and todorokite nanowires, respectively, which were used to measure the diameter of the assembled nanowires.

composition of $\alpha$-MnO$_2$ and todorokite nanowires was evaluated to be K$_{0.11}$MnO$_2$ and Mg$_{0.20}$MnO$_2$, respectively, indicating the different amounts of stabilizing cations present in each structure.

Figures 3(e) and 3(f) show representative AFM images of single nanowires of $\alpha$-MnO$_2$ and todorokite assembled on the nanofabricated platform using DEP. While the AFM images show the devices after their top-side clamping using EBID of Pt, which appear as metallic bumps that run across the length of the nanowires at their distal ends, the respective SEM images taken prior to Pt deposition are shown in the inset of these images. Apart from securing the nanowires in place on top of the gold assembly electrodes, the Pt metallization serves to improve the electrical contact to the nanowires through a reduction of the contact resistance at the metal-nanowire interface. The diameter of the assembled nanowires was obtained from AFM height plots, which are obtained from the tapping mode micrographs of Figures 3(e) and 3(f). These are shown in panels “g” and “h” for the $\alpha$-MnO$_2$ and todorokite nanowire devices, respectively. From these plots, the diameters of the $\alpha$-MnO$_2$ and todorokite nanowire devices are obtained as 34 nm and 62.6 nm, respectively.

Figures 4(a) and 4(b) show the I-V measurements performed on the $\alpha$-MnO$_2$ and todorokite nanowire devices, respectively. The top panel in Figure 4(a) shows a representative I-V plot obtained from single $\alpha$-MnO$_2$ nanowire. This nanowire (as well as others from this material system) exhibits a non-linear current vs. voltage relationship, indicating the presence of a Schottky barrier at the metal-nanowire interface. The two-terminal resistance of the nanowire, $R_{2T}$, is given by the following equation:

$$R_{2T} = \frac{l}{\sigma A} + 2R_C,$$

(1)

where “$\sigma$” represents the electronic conductivity, “$R_C$” represents the nanowire-metal contact resistance, “$l$” represents the suspended length of the nanowire device, “$d$” its diameter, and “$A$” its cross-sectional area ($= \pi d^2/4$). The two-terminal resistance of four different nanowire samples from this material phase, which is computed as the ratio of a differential change in voltage with respect to the current at a 1 V bias, is plotted in the bottom panel of Figure 4(a) as a function of the nanowire length to area ratio (i.e., $l/A$). The linear-fit to these experimental data from four different nanowire samples is then used to extract both the values of the electronic conductivity, which is intrinsic to the material system, and the nanowire-metal contact resistance for these four nanowire samples. From Equation (1), the slope of this plot indicates the inverse of the nanowire electronic conductivity (i.e., its resistivity) and the y-axis intercept indicates the total device contact resistance (half of which represents the contact resistance at each contact). From this method, we obtain an electronic conductivity and contact resistance of 2.259 S/cm and 395.7 k$\Omega$, respectively. It is important to note
that these values, which represent the average values obtained from the four measured samples, are near the previously reported values of 1.822 S/cm (our report in Ref. 14).

The I-V plot obtained from a representative nanowire device involving the todorokite phase is shown in the top panel of Figure 4(b). From this plot (as well as from other measured device within this phase), it can be seen that the I-V relationship is linear and indicates the establishment of an ohmic contact at the nanowire-metal interface. The two-terminal resistance of four different todorokite nanowire devices is plotted as function of l/A in the bottom panel of Figure 4(b). From the linear fit to these data, we obtain the electronic conductivity and contact resistance for this material system to be $4.9 \times 10^{-2}$ S/cm and 21.7 MΩ, respectively. Thus, we find that the electronic conductivity of the todorokite phase is smaller than α-MnO$_2$ by a factor of ∼46.

The electronic conductivity values obtained via this single-nanowire measurement method are significantly larger than those reported in the past for films consisting of tunnel structured manganese oxides.$^{37,38}$ These reports have indicated electronic conductivity to be on the order of $10^{-3}$-$10^{-4}$ S/cm for α-MnO$_2$ and on the order of $10^{-6}$ S/cm for todorokite. However, these values were determined via a four point probe method performed on electrode films. Because grain boundary resistance or the presence of film additives does not affect our measurement method, we obtain significantly higher electronic conductivity values. In addition, past work has reported that the electronic conductivity of α-MnO$_2$ was anisotropic in nature, with the conduction in the direction parallel to tunnel growth being greater than the direction perpendicular to tunnel growth.$^{39}$ This provides further reason for the greater electronic conductivity values obtained in this work since our measurements are performed solely along the direction parallel to tunnel growth. These values obtained via the single nanowire platform are thus believed to be a better representation of the electronic conductivity, which is intrinsic to these manganese oxide materials. A summary of the important properties of α-MnO$_2$ and todorokite discussed thus far is shown in Table I.

The rate performance of these materials at various current rates in a Li-ion battery is shown in Figure 5. In this electrochemical test, the magnitude of the applied current is incrementally increased every five cycles while the specific capacity of the material is recorded. If higher fractions of the initial capacity remain at higher current magnitudes, the electrode material exhibits higher power density in a Li-ion battery. Since the two studied materials have different theoretical capacities, the capacities at each current rate are normalized by the first discharge capacity of the respective
TABLE I. Comparison of important properties for $\alpha$-MnO$_2$ and todorokite. Note that a range of $D_{Li^+}$ values are given for the fully charged (delithiated) to the fully discharged (lithiated) state.

<table>
<thead>
<tr>
<th>Material</th>
<th>Chemical formula</th>
<th>Tunnel size$^{20}$</th>
<th>$D_{Li^+}^{20-22}$</th>
<th>Intrinsic electronic conductivity (measured)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-MnO$_2$</td>
<td>K$_{0.11}$MnO$_2$</td>
<td>4.6 Å × 4.6 Å</td>
<td>$10^{-10}$-$10^{-11}$ cm$^2$/s</td>
<td>2.259 S/cm</td>
</tr>
<tr>
<td>Todorokite</td>
<td>Mg$_{0.20}$MnO$_2$</td>
<td>6.9 Å × 6.9 Å</td>
<td>$10^{-7}$-$10^{-10}$ cm$^2$/s</td>
<td>$4.9 \times 10^{-2}$ S/cm</td>
</tr>
</tbody>
</table>

material so that a comparison can be made on the percent of initial capacity maintained through cycling. Despite its smaller crystal tunnels, on first discharge (at the slowest current rate), $\alpha$-MnO$_2$ exhibits a much greater capacity of 265 mAh/g compared to 148 mAh/g for todorokite. However, as the current rate is increased, todorokite exhibits superior performance. At the second current rate of $C/20$, todorokite maintains over 80% of its initial capacity, while $\alpha$-MnO$_2$ maintains less than 60% of its initial capacity. This trend continues at each successive current rate. At the highest rate of 1C, todorokite has a discharge capacity of 65 mAh/g, corresponding to 43% of its initial capacity. $\alpha$-MnO$_2$ has a much lower capacity of 25 mAh/g at this rate, maintaining only 10% of its initial capacity. As the current rate is increased and charge is forced into and out of the electrodes at a higher rate, the electrochemical performance of $\alpha$-MnO$_2$ (in terms of specific capacity and fraction of initial capacity maintained) decreases at a much quicker rate and to a much lower value than that for todorokite. Furthermore, since in manganese oxides there is a large capacity loss from first to second cycle, we also normalize by the second discharge capacity for each material (see Figure S2 of the supplementary material for the rate performance of both materials normalized by the second discharge capacity$^{30}$). However, the same trend in performance is observed, with todorokite manganese oxide showing superior high rate characteristics.

While it is well known that rate performance of a battery material depends on many factors$^7$ (e.g., diffusion distances, chemical composition, and physical structure), the similar chemistry, crystal structure, morphology, and surface structure of $\alpha$-MnO$_2$ and todorokite MnO$_2$ allow for nearly all variables except for electronic and ionic conductivity to be held constant in this study during electrochemical cycling. Therefore, this comparison of the rate performance of these two manganese oxide polymorphs in a Li-ion battery provides insight into the contributions of intrinsic electronic conductivity.

FIG. 5. Electrochemical performance of $\alpha$-MnO$_2$ and todorokite nanowires in a Li-ion battery at current rates of $C/50$, $C/20$, $C/10$, $C/2$, and 1C. (a) and (b) show the capacity of $\alpha$-MnO$_2$ and todorokite nanowires, respectively, versus the cycle number as a function of applied current density. The galvanostatic discharge/charge curves are shown for the first cycle at each current rate for $\alpha$-MnO$_2$ (c) and todorokite (d).
and ionic conductivities in this class of materials. The superior electrochemical performance of todorokite at higher current rates over $\alpha$-MnO$_2$ corresponds to the higher ionic conductivity of the todorokite crystal structure, which is three orders of magnitude higher than that of $\alpha$-MnO$_2$. At the same time, electronic conductivity does not seem to be as important of a factor at these current rates since the electronic conductivity of $\alpha$-MnO$_2$ is much higher than that of todorokite (by a factor of $\sim$46). Thus, ionic conductivity is playing a more significant role than electronic conductivity in fast electrochemical cycling for tunnel structured manganese oxides, and it can then be assumed that Li-ion diffusion is the limiting factor in tunnel structured manganese oxides at higher current densities. Past reports have stated that the intrinsically low electronic conductivity of manganese oxide materials resulted in poor rate performance, but we find that this is not the case, with our results indicating that ionic conductivity is in fact more important. The performance of these materials is governed by how fast $\text{Li}^+$ ions can be transported through the tunnel structure rather than the rate at which electrons can be conducted through the lattice. Thus, by tuning the tunnel size and the stabilizing cation, the ionic and electronic conductivities of these tunnel structured materials can be tailored for improved electrochemical rate performance in Li-ion batteries. These same principles apply to the use of these materials in emerging energy storage systems based on other charge-carrying ions such as Na-ion, K-ion, Mg-ion, and Al-ion batteries.

Although these findings challenge previous reports on manganese oxides, they are in agreement with past reports on other materials that suggest that as long as electronic conductivity is above a threshold value, ionic conductivity is the dominating factor for performance at higher current rates. Referring back to the case of LiFePO$_4$, because of the low electronic conductivity, this material required special approaches to be combined with carbon in order to improve electronic conductivity and achieve efficient electrochemical performance. The approach outlined in this work allows for the quantification of the electronic conductivity of a material and can be used to identify a value above which electronic conductivity needs to be increased in order to achieve the maximum possible electrochemical performance. This method can be applied to both anode and cathode materials that are mixed electronic and ionic conductors and may be particularly attractive for materials such as LiFePO$_4$ that show high ionic conductivities but are limited by their low electronic conductivities. Further, utilization of this approach can be extended to developing electrode materials for energy storage systems beyond Li-ion batteries where ionic conductivity may become limiting due to the larger, heavier, and/or multivalent nature of alternative charge-carrying ions.

In summary, the relationship between electronic conductivity, ionic conductivity, and rate performance in Li-ion batteries was evaluated for two manganese oxide polymorphs. The crystal structures of the two materials studied, $\alpha$-MnO$_2$ and todorokite manganese oxide, are characterized by tunnels with different square dimensions that are stabilized by different cations ($\text{K}^+$ and $\text{Mg}^{2+}$ for $\alpha$-MnO$_2$ and todorokite phases, respectively). Therefore, the two materials exhibit differing electronic and ionic conductivities. A single nanowire DEP-assisted nanofabricated platform was utilized to measure the electronic conductivity of each material, and it was found that the electronic conductivity of $\alpha$-MnO$_2$ was two orders of magnitude higher than that of todorokite. However, todorokite manganese oxide showed better electrochemical performance at higher current rates, with todorokite maintaining 43% of its initial capacity when the current was increased from C/50 to 1C while $\alpha$-MnO$_2$ maintained only 10% of its initial capacity. This improved performance of todorokite nanowires was attributed to its greater ionic conductivity than that of $\alpha$-MnO$_2$ nanowires, allowing for quicker diffusion of the charge-carrying $\text{Li}^+$ ions. These results indicate that in tunnel structured manganese oxides, the ionic conductivity is more important for electrochemical performance at high current rates, which is contrary to previous reports on manganese oxides that state electronic conductivity limits high rate performance. Therefore, by adjusting the tunnel size and the charge/size of the stabilizing cation, the conductivities of manganese oxides with tunnel crystal structures can be tuned for improved electrochemical performance at high current rates. This approach of evaluating the electronic and ionic conductivities of a material and their relationship to rate performance can provide a useful perspective on identifying and evaluating electrode materials for use in intercalation based energy storage systems. Further, as many mechanical systems become significantly smaller in size, such as in microelectromechanical systems (MEMS), energy storage devices based on single nanostructures
may become very attractive, and this method provides an excellent platform for studying the electronic properties of materials for nanostructured devices.

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30 See supplementary material at http://dx.doi.org/10.1063/1.4948272 for the relative sizes of structural tunnels with respect to the size of lithium ion and for the rate performance of the materials normalized by the second discharge capacity.


