Anomalous Pseudocapacitive Behavior of a Nanostructured, Mixed-Valent Manganese Oxide Film for Electrical Energy Storage

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Supporting Information

ABSTRACT: While pseudocapacitors represent a promising option for electrical energy storage, the performance of the existing ones must be dramatically enhanced to meet today’s ever-increasing demands for many emerging applications. Here we report a nanostructured, mixed-valent manganese oxide film that exhibits anomalously high specific capacitance (≈2530 F/g of manganese oxide, measured at 0.61 A/g in a two-electrode configuration with loading of active materials ≈0.16 mg/cm²) while maintaining excellent power density and cycling life. The dramatic performance enhancement is attributed to its unique mixed-valence state with porous nanoarchitecture, which may facilitate rapid mass transport and enhance surface double-layer capacitance, while promoting facile redox reactions associated with charge storage by both Mn and O sites, as suggested by in situ X-ray absorption spectroscopy (XAS) and density functional theory calculations. The new charge storage mechanisms (in addition to redox reactions of cations) may offer critical insights to rational design of a new-generation energy storage devices.

KEYWORDS: Energy storage, electrochemical capacitors, mixed-valent compounds, enhanced pseudocapacitance, in situ X-ray absorption spectroscopy

While the application of existing batteries is often limited by low power, short cycle life, and long charging time,¹ the use of conventional capacitors suffers from inadequate energy density. Pseudocapacitors may bridge the gap between batteries and capacitors.² Unlike electrochemical double layer capacitors (EDLCs), which store electrical energy by accumulation of ions on electrode surface,³ pseudocapacitors make use of fast redox reactions or phase changes on the surface or subsurface of electrodes,⁴–⁶ offering much higher energy densities than EDLCs. However, the rate capability and cycling stability of pseudocapacitors are perceived to be inferior to those of EDLCs and the energy density to be much lower than those of available batteries. To overcome these limitations, considerable efforts have been devoted to the creation of new...
materials for pseudocapacitors. To date, however, the progress has been hindered largely by the lack of a profound understanding of the complex charge storage mechanisms related to intercalation of ions into electrode materials (of layered or channeled structures), reaction of ions with active electrode materials (to form new phases), and/or electrochemical adsorption of ions on electrode surfaces. It is traditionally believed that the pseudocapacitive behavior is associated primarily with the redox reactions of the cations (or changes in oxidation states of the cations) in electrode materials during operation. 2 A suitable electrode material for high performance should promote fast, reversible redox reactions on the surface or subsurface. 3,4

Among many materials investigated, since first reported by Goodenough group, 7 MnO2 has attracted much attention because it is abundant, inexpensive, and environmentally benign. While MnO2 has high theoretical capacitance (~1370 F/g as the oxidation state of Mn ion is changed from 4+ to 3+ over a potential window of 0.8 V), its poor electronic conductivity often limits the electrode utilization; only the surface layers may participate in redox reactions. To overcome this limitation, MnO2 has been mixed with carbon particles or loaded onto carbon supports (including carbon nanotubes and graphene). 5 To date, however, the reported specific capacitance of MnO2 varies from ~150 to ~940 F/g while the cycling stability still needs further improvement. Although higher specific capacitance (~1145 F/g) has been reported, 17 the MnO2 was deposited into a nanoporous gold film (~100 nm thick) and thus could be less competitive economically for practical applications. Further, the rate capability is still unsatisfactory for large-scale applications such as auxiliary power units for electric vehicles. With several oxidation states and a wide range of phases, manganese is a vital component in photosynthetic systems due to its unique ability to cycle between various oxidation states. 18 In particular, manganese oxides can assume many different crystal structures upon accommodation of other metal cations. These complex features often give rise to unusual properties of manganese oxide. For example, the dramatic enhancement of catalytic activities toward oxidation of various organic compounds was attributed to the mixed-valence of manganese oxides. 19,20

Figure 1. Electron microscopy analysis. (a) SEM image of carbon fiber paper (CFP) before coating showing 3D interconnected, porous structures. (b) SEM image of a carbon fiber before coating. (c) SEM image of a carbon fiber after conformal coating of MnO2 for 30 min. (d) SEM image of the MnO2 coating annealed at 400 ºC in air for 2 h. (e) TEM image of MnO2 coating annealed at 400 ºC in air for 2 h. (f) A zoomed-in view of the blue square area in (e) showing a cluster of the needle-shaped crystals with diameters of ~3 to ~4 nm. (g) High-resolution TEM images showing the fringes of Mn3O4 and α-Mn2O3 phase.
that determine their unique properties are the “electronic coupling” between the two redox sites, and the “reorganization energy” associated with electron transfer between them.\textsuperscript{21} Charge localization or delocalization has been a central issue in mixed-valence chemistry. By a classification scheme proposed by Robin and Day,\textsuperscript{22} mixed-valent compounds can be completely localized, fully delocalized, or systems in between, depending on the strength of the electron interaction between the oxidized and reduced sites. To date, compounds of group 8–11 transition metals have been most intensively studied. In particular, compounds of iron, ruthenium, platinum, and copper have been widely studied.\textsuperscript{23} For example, many mixed-valent copper-based oxides have been developed as superconductors. The compound YBa$_2$Cu$_3$O$_7$ has mixed-valent Cu(II) and Cu(III). Also, a number of rare-earth compounds with atomic-like f levels coexisting with wide s–d band at the Fermi level have shown very unique thermal and magnetic properties.\textsuperscript{24}

However, the nature of the mixed-valent chemistry on the surface of nanostructured materials has not yet been fully understood and a fundamental understanding of the relationship between mixed-valent structure and properties is still lacking. It should be also noted that the mixed-valence chemistry of the early transition metals is considerably less well established, yet a remarkable variety of structurally diverse mixed-valence compounds can be formed from these elements. Their wide range of oxidation states, coordination numbers, and geometries can offer great potential for the formation of unique mixed-valent compounds, and many of these may exhibit distinctive bonding, chemistry, and properties suitable for various applications. In particular, although early transition elements such as titanium, vanadium, and manganese are important in biology, catalysis, artificial photosynthesis, and energy storage/conversion science, the controlled synthesis of their mixed-valent compounds and their unique electrochemical properties have not yet been explored. In this paper, we demonstrated the controlled synthesis of nanostructured, mixed-valent manganese oxides and explored their unique properties as electrodes for high-performance pseudocapacitors.

We used conductive and porous carbon fiber paper (CFP) as both the current collector and the electrode for conformal coating of mixed-valence MnO$_x$, as the active electrode material for pseudocapacitors (Figure 1a,b). Individual carbon fibers in the CFP are well-connected and the pores are sufficiently large to allow efficient ion access to all surface area of the electrode. We deposited a thin, uniform coating of nanoporous MnO$_x$ directly onto porous CFP using a simple precipitation method in an aqueous solution at 75 °C (Figure 1c,d). The porous network structure of the CFP is retained because the conformal MnO$_x$ coating is relatively thin, as revealed by microscopy. The MnO$_x$ coated CFP were then heat-treated at 200–450 °C in different atmospheres (air, N$_2$, and 4% H$_2$). TEM analysis of the samples annealed at 400 °C in air for 2 h revealed that the MnO$_x$ films consist of many low aspect-ratio crystals (each being a few tens of nanometers in size) as well as clustered and needle-shaped crystals, whose diameters vary from a few nanometers to ~10 nm (Figure 1e–g, Supporting Information S1). Selected area electron diffraction (SAED) analysis (Supporting Information Figure S1b) suggested that the low-aspect ratio nanocrystals examined are α-Mn$_2$O$_3$ with a lattice constant of 0.94 nm, and the needle-shaped crystals were identified as Mn$_3$O$_4$ (Hausmannite) based on lattice images (Figure 1g). The lattice fringes reveal the axes of the two

needle-shaped Mn$_3$O$_4$ crystals are parallel to the (101) lattice planes (Supporting Information Figure S1c). Since both the (101) and (011) spacing are the largest lattice spacing in the Mn$_3$O$_4$ lattice, such an orientation may facilitate the incorporation and transport of ions along this direction. The thickness of MnO$_x$ coating varied from ~70 to ~800 nm (Supporting Information Figure S2–S4), depending on the deposition time (2 to 30 min).

To further characterize the structural features of the MnO$_x$ coatings formed on CFP, we used both laboratory and synchrotron-based X-ray diffraction (XRD) analysis. Figure 2a

shows the synchrotron-based XRD patterns (transmission mode) of samples (deposited for 30 min) before and after annealing in air at different temperatures (200 and 400 °C) in air for 2 h. (b) Enlarged view of XRD pattern between 16–19° of XRD pattern of MnO$_x$ annealed at 400 °C in air for 2 h and highlighted in Figure 2a. (c) XRD pattern at of MnO$_x$ annealed at 400 °C in air for 2 h measured at different incident angle (0.1–1°). (d) XRD pattern at incident glancing angle of 0.1° of MnO$_x$ annealed at 400 °C in air for 2 h showing the representative surface species.
Figure 2a,b. These crystalline phases started to appear at ∼360 °C when the temperature was raised from 200 to 400 °C in air, as revealed by the in situ XRD analysis (Supporting Information Figure S5). It is noted, however, that the transmission-mode XRD pattern is quite different from those collected at a small glancing angle (Supporting Information Figure S6), suggesting that the phases on the surface are very different from those in the bulk.

To gain some insights into the structures of the surface layer, we collected XRD patterns at different glancing incident angles (Figure 2c,d). A lower incident angle corresponds to a shallower penetration depth of the X-ray, allowing us to probe the structure of a layer closer to the surface. When the incident angle was varied from 1 to 0.1°, the α-Mn₂O₃ peaks decreased gradually while the peaks corresponding to K-incorporated MnO₂ (K₀.₆MnO₂ and K₀.₅₁Mn₀.₉₃O₂) and Mn₅O₈ increased considerably, suggesting that α-Mn₂O₃ is present predominantly in the bulk whereas the K-incorporated MnO₂ and Mn₅O₈ are formed mostly near the surface (Figure 2d). It is noted that small peaks corresponding to Mn₃O₄ were observable in both transmission-mode and glancing angle mode XRD patterns, implying that small amount of Mn₃O₄ is present in the bulk and on the surface. This is consistent with TEM observation (Figure 1g). The surface phases (K-incorporated MnO₂, Mn₅O₈, and Mn₆O₁₈) were formed at 400 °C, as indicated by the low glancing angle XRD analysis at different temperatures (Supporting Information Figure S7).

XRD analysis of the mixed-valent MnOₓ of different thicknesses suggests that the predominating phase of the ∼800 nm films (deposited for 30 min) was α-Mn₂O₃ whereas that of the ∼70 nm films (deposited for 2 min) was Mn₃O₄ which showed the highest specific capacitance. As the thickness was reduced (Supporting Information Figure S8), the predominating “bulk” phase was changed from α-Mn₂O₃ to a phase similar to Mn₂O₃. This is anticipated because the degree of MnO₂ reduction (by the carbon substrate) decreases in the direction away from the carbon substrate surface, which was exposed to air. The annealing condition created a gradient in oxidation state of Mn ion along the thickness direction; thinner MnOₓ films deposited on carbon fiber were more reduced. However, they were still mixed-valent MnOₓ and there is more Mn₃O₄ phase in a thinner film (Supporting Information Figure S8−S10). It is noted that all electrodes deposited for 2, 5, 15, and 30 min have the same surface phases; the graded oxidation state remained largely the same.

Gas adsorption/desorption analysis implied that the microstructure of MnOₓ underwent a dramatic rearrangement during the annealing process, producing porous, nanostructured MnOₓ (Supporting Information Figure S11). The specific surface area increased from 5.21 m²/g for amorphous MnO₂ to 261.8 m²/g for the multivalent MnOₓ as the pore volume increased from 0.021 to 0.149 cm³/g (∼42% porosity) at the same time. The formation of tubed structure of K-incorporated MnO₂ on the surface may partially account for enlarged surface area and pore volume.18,18 The porous, nanostructured multivalent MnOₓ is ideally suited for fast mass and charge transfer associated with energy storage processes.

To evaluate the characteristic behavior of the mixed-valent MnOₓ electrodes for electrical energy storage, we performed several electrochemical measurements in a 1 M Na₂SO₄, 1 M H₂SO₄ electrolyte solution.
solution. The mixed-valent MnO₂ electrode showed excellent "square-shape" cyclic voltammograms at 50 mV/s (Figure 3a) with current densities being almost 1 order of magnitude higher than those of the amorphous MnO₂ electrode. The symmetric shape and the instant response upon the reversal of voltage indicate that surface reactions are highly reversible and very fast. It is noted that the contribution of the porous carbon fiber substrate to the capacitance is negligible.

We have also measured the internal resistance of the electrochemical capacitors when the potentials were reversed (Supporting Information Figure S12) and plotted them as a function of applied current densities (Figure 3b). The slopes of the plots correspond directly to the equivalent series resistances (ESR) of the capacitors. This internal resistance critically influences the power density (or rate capability) of electrochemical capacitors; low capacitance and deviation from ideal capacitor behavior are usually associated with large ESR. It is clearly shown that the mixed-valent MnO₂ displayed much smaller ESR than the amorphous MnO₂, at a given current density due most likely to enhanced rates of the surface redox reactions. This observation was further confirmed by the impedance measurements (insert of Figure 3b). The charge-transfer resistance (the diameter of the semicircle in the impedance spectrum) of the mixed-valent MnO₂ was much smaller than that of the amorphous MnO₂. The long tail at low frequencies of the mixed-valent MnO₂ is closer to a vertical line for an ideal capacitor, another indication that the mixed-valent MnO₂ has higher capacitance and lower resistance than the amorphous MnO₂.

Typical charge-discharge curves at a constant current of 0.61 A/g are shown in Figure 3c. The "linear" and symmetrical charge-discharge curves indicate again high Coulombic efficiency or excellent reversibility. The specific capacitance (calculated from the discharge curve) of the amorphous MnO₂ was 333 F/g, comparable to the values reported in the literatures. In contrast, the specific capacitance for the mixed-valent MnO₂ (of ~70 nm thick) was ~2530 F/g, almost eight times higher than that of the amorphous MnO₂ (of the same loading). This represents the highest specific capacitance ever reported among all known pseudocapacitor materials, including MnO₂ (1145 F/g; film <40 nm thick in a 100 nm porous Au film), Ni(OH)₂ (1335 F/g; nanoplates <10 nm thick), and RuO₂ (1340 F/g; nanodots with 2–3 nm in diameter) when all normalized to the weight of the active material only.

Because high rate capability is the most important feature of electrochemical capacitors, we measured the performance at very high cycling rates. Typically, the capacitance of a pseudocapacitor may decrease with operating current density due to mass transport limitations, especially when insertion (or removal) of ions into (or from) the electrode subsurface is involved. Much to our surprise, however, the capacitance of the mixed-valent MnO₂ was not kinetically limited even at very high cycling rates (Supporting Information Figure S13), demonstrating ~2430 F/g at 122.7 A/g. Further, the mixed-valent MnO₂ electrode displayed remarkable long-term cycling stability; cyclic voltammograms collected after 100 000 and 200 000 cycles (Figure 3d) showed little change, whereas the capacitance of the amorphous MnO₂ was much lower and degraded considerably during cycling (Supporting Information Figure S14–15). It was also found that symmetric pseudocapacitors constructed from the mixed-valent MnO₂ showed very stable performance up to 1.0 V (Supporting Information Figure S16).

It is noted, however, that the specific capacitance drops with the thickness of the MnO₂ film (or loading), suggesting that only a thin film was fully utilized (or the nanoporous surface phases make dominating contributions to the observed capacitance) (Supporting Information Figure S17–18). This is not surprising because the charge storage in a capacitor is primarily confined to the surface and subsurface (or a thin layer). To increase the performance of electrochemical capacitors by increasing the film thickness of active materials is proven ineffective and, perhaps, fundamentally unattainable; after all, the rate capability may ultimately diminish with film thickness. However, our results demonstrate that it may be unnecessary to increase film thickness because the charge storage capacity of the MnO₂ film can be dramatically enhanced (~8 times) by creating mixed-valent nanostructure, achieving values much higher than the "theoretical capacity" previously believed (e.g., ~1370 F/g for MnO₂ under similar conditions). Indeed, the estimated specific energy density of the ~70 nm thick mixed-valent MnO₂ film (single electrode in a voltage window between 0 and 1.0 V) reached ~352 Wh/kg at a power density of ~614 W/kg and showed little dependence on cycling rate, still retaining ~337 Wh/kg at power densities up to ~117 800 W/kg (full charge or discharge in 10 s) when all normalized to the weight of active material only. The demonstrated specific energy densities of single electrode are much higher than those of the state-of-art pseudocapacitor materials. (Note the voltage window for MnO₂ and Ni(OH)₂ were 0.8 and 0.55 V in two- and three-electrode configuration, respectively) and even comparable to those of high-performance battery materials such as FePO₄ nanowires (~300 Wh/kg at ~4000 W/kg) and Li(Ni₀.₅Mn₀.₅)O₂ (~600 Wh/kg at ~6000 W/kg) while retaining much higher gravimetric power (when all normalized to the weight of the electrode material only). Although significantly improved performance has been achieved in this study with a nanoscale coating, the mixed-valent MnO₂ shows great potential to provide an order of magnitude increase in practical energy density of electrochemical capacitors without penalizing power density. We believe that MnO₂ coatings must be thin to offer the best possible power density. Therefore, one effective approach to increasing practical energy density (e.g., loading) without compromising the specific capacitance or rate capability is to use nanocarbon fibers, thus increasing the surface area of CFP for conformal coating of MnO₂.

The phase composition and nanostructure of the electrode material is very sensitive to the annealing conditions. For example, when the annealing temperature was increased from 400 to 450 °C (but still in air for 2 h), XRD analysis suggested that the Mn₃O₄ phase was converted to α-Mn₃O₄ (Supporting Information Figure S19). Similarly, when the annealing atmosphere was changed from air to N₂ and 4% H₂ balanced with Ar (still at 400 °C for 2 h), the as-synthesized amorphous MnO₂ on CFP was converted to pure Mn₃O₄ and a mixture of MnO and Mn₃O₄, respectively (Supporting Information Figure S20). Further, the amorphous MnO₂ powder sample (synthesized under the same conditions but without carbon support) remained amorphous when annealed at 400 °C, but transformed to crystalline α-Mn₃O₄ when annealed at 500 °C, in air for 2 h in the absence of carbon (Supporting Information Figure S21). Electrodes made of these phases performed poorly, far inferior to that of the electrodes made of the
multivalent MnO\textsubscript{x} created by annealing in air at 400 °C for 2 h (Supporting Information Figure S19–S20).

Since the mixed-valent phases seem to play a pivotal role in achieving the anomalously high capacitance, we performed both ex situ and in situ XAS to gain some insights into the charge-storage mechanism of the mixed-valent MnO\textsubscript{x} electrodes (Supporting Information Figure S22–S23). The in situ X-ray absorption near edge spectroscopy (XANES) spectra (Figure 4a) for the as-synthesized MnO\textsubscript{2} electrodes acquired during the first discharge (0.8 to −0.8 V) showed an entire edge shift toward lower energy in a continuous manner, suggesting that the charge storage is mostly associated with the Mn\textsuperscript{3+/4+} redox reactions, as conventionally believed. In contrast, however, the XANES spectra (Figure 4b) for the mixed-valent MnO\textsubscript{x} collected under the identical conditions (except over a wider voltage window from 1.0 to −1.0 V) showed completely different spectral features that have never before been reported. First, there was no obvious entire edge shift during discharge, although a slight edge shift toward lower energy was observed, indicating a decrease in average oxidation state of Mn ions. The average change in Mn valence (calculated from the edge shift) for both cases was similar: ~0.3 within a voltage window of 0.0 to 0.8 V (Supporting Information Figure S23); yet, the observed specific capacitance for the mixed-valent MnO\textsubscript{x} is much higher (~8 times) than that for the as-prepared MnO\textsubscript{2} sample. Clearly, the change in oxidation state of Mn ion cannot account for the anomalous pseudocapacitive behavior. Second, the dominating spectral feature is a unique evolution of the shoulder peak (B), which is related to the ligand-to-metal charge transfer (LMCT) process. The increased B peak intensity indicates the increased degree of covalent character of Mn(3d)-O(2p) bonding during the discharge. Thus, the unique Mn K-edge change in the form of increasing B feature clearly shows that a large portion of the charge compensation might be originated from the hole state redistribution toward the oxygen sites, rather than just the reduction of Mn ion (as seen for the as-synthesized MnO\textsubscript{2}), suggesting that the unique atomic and electronic structure (Supporting Information Figure S22) of the nanostructured, mixed-valent MnO\textsubscript{x} may allow additional charge compensation mechanism, which has not been observed in MnO\textsubscript{2}. Although small intensity change of B feature in XANES spectra during charge−discharge were reported in the literature\textsuperscript{34,35} for transition metal K-edges such as Co and Mn, it has never before been observed that...
These spectral changes (LMCT) play a dominating role over the continuous edge shift (redox reaction of cations).

The role of oxygen anions for charge compensation in transition metal oxides is not unprecedented; it was previously argued for lithium battery electrodes. Aydinol et al. showed that more charge can be transferred to the oxygen anions than to the metal cations in the oxide upon intercalation of lithium ions. To estimate the charge distribution in the nanoporous multivalent \( \text{Mn}_3\text{O}_4 \) (with dominant phase of \( \text{Mn}_2\text{O}_4 \)), we resorted to spin-polarized density functional theory (DFT) calculations. To model the geometry of \( \text{Mn}_3\text{O}_4 \) nanoneedles (as seen in Figure 1g), we used a tetragonal slab of \( \text{Mn}_3\text{O}_4 \) exposing to the vacuum two opposite (001) surfaces of area \( 5.94 \times 5.94 \text{ Å}^2 \) and having a linear dimension perpendicular to the surface of 19.5 Å. Our DFT calculations (Figure 4c) show that significant amount of the excess negative charge is indeed accumulated at the surface of the \( \text{Mn}_3\text{O}_4 \) nanoneedles. In the bulk, the excess negative charge gradually decays from the surface peak, localizing prevalently in correspondence of the Mn\(^{3+}\) ions in the \( \text{MnO}_6 \) octahedra rather than at the Mn\(^{2+}\) centers in the \( \text{MnO}_4^2- \) tetrahedra. An analysis of the individual Bader atomic charges shows, in particular, that the percentage of excess charge stored at the surface and in the bulk of \( \text{Mn}_3\text{O}_4 \) is 36 and 64%, respectively, while in the bulk the negative charge accumulated at or in proximity of Mn\(^{2+}\), Mn\(^{3+}\), and O centers is 15, 50, and 35%, respectively.

Our DFT calculations therefore suggest that the amounts of excess charge accumulated on the surface and at O centers are significant, consistent with our in situ XAS results. Charge accumulation on O centers appear to be favored by the close proximity of the Mn\(^{3+}\) species that, thanks to the good hybridization of the Mn\(^{3+}\) 3d and the O 2p orbitals, spill the excess negative charge onto the neighboring O atoms. These new charge compensation mechanisms at O centers and surfaces directly challenge the traditional notion that pseudocapacitance is primarily associated with redox reaction of cations.

Additionally, the coexistence of aliovalent cations (Mn\(^{2+}\), Mn\(^{3+}\), and Mn\(^{4+}\)) may facilitate the formation of more ionic defects (e.g., vacancies and misplaced ions) and electronic defects (electrons and holes), thus altering the electronic, ionic, and catalytic properties of the manganese oxides. These defects may accelerate the kinetics of the surface redox reactions. Also, the mismatches induced by structural differences among different manganese oxide phases may produce additional defects (cavities, stacking faults, etc.), thus facilitating the formation of porous nanoarchitectures that may enhance the transport of charged species and extend the reaction sites from the surface to the subsurface of electrode. Recent theoretical studies predicted that photocatalytic activity of MnO\(_2\) can be enhanced by introducing Ruetschi defects or protonated Mn(IV) vacancies, suggesting that electronic properties can be tailored by tuning the defect structure during synthesis.  

Our results suggest that electrochemical capacitors based on this MnO\(_2\) film have potential to reach energy densities much higher than those of existing pseudocapacitors while maintaining high rate capabilities and excellent cycling performance of EDLCs. This can be accomplished by the creation of thin films of mixed-valent manganese oxides with porous nanoarchitechture, enabling multiple charge storage mechanisms with much smaller internal resistance and highly reversible, faster charge transfer kinetics. Although we have focused on MnO\(_2\) as active materials for pseudocapacitors in this study, other transition metal oxides could also be explored using a similar method to design mixed-valent nanoarchitectures/carbon composites with significantly enhanced electrochemical performances for other applications.

## ASSOCIATED CONTENT

### Supporting Information

Additional figures and experimental details are included. This material is available as free of charge via the Internet at [http://pubs.acs.org](http://pubs.acs.org).

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### Notes

The authors declare no competing financial interest.

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## REFERENCES


(33) Kang, K. S.; Meng, Y. S.; Breger, J.; Grey, C. P.; Ceder, G. Science 2006, 311 (5763), 977−980.