Rescaling of metal oxide nanocrystals for energy storage having high capacitance and energy density with robust cycle life

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Nanocrystals are promising structures, but they are too large for achieving maximum energy storage performance. We show that rescaling 3-nm particles through lithiation followed by delithiation leads to high-performance energy storage by realizing high capacitance close to the theoretical capacitance available via ion-to-atom redox reactions. Reactive force-field (ReaxFF) molecular dynamics simulations support the conclusion that Li atoms react with nickel oxide nanocrystals (NiO-n) to form lithiated core–shell structures (Ni:Li$_2$O), whereas subsequent delithiation causes Ni:Li$_2$O to form atomic clusters of NiO-a. This is consistent with in situ X-ray photoelectron and optical spectroscopy results showing that Ni^{2+} of the nanocrystal changes during lithiation–delithiation through Ni^0 and back to Ni^{2+}. These processes are also demonstrated to provide a generic route to rescale another metal oxide. Furthermore, assembling NiO-a into the positive electrode of an asymmetric device enables extraction of full capacitance for a counter negative electrode, giving high energy density in addition to robust capacitance retention over 100,000 cycles.

rescaled atomic clusters | metal oxide nanocrystals | energy storage | molecular dynamic simulation | in situ electrochemical spectroscopy

The most critical challenge in energy storage is maximizing capacitance along with high power density and long cycle life. High-power capacitors (1–4) are candidates to meet this challenge, and can be classified into two categories: (*i*) energy storage systems where charge is stored in electrochemical double layers (EDLs) (5, 6) and (*ii*) pseudocapacitors that store charge by redox reactions (7–14). Unfortunately, EDLs have low capacitance, whereas metal oxide pseudocapacitors lead to short cycle life. Furthermore, typical capacitors have low energy density (5, 10). In principle, the capacitances of metal oxide crystals can be fully obtained via ion-by-atom surface redox reactions. A capacitor that enables high capacitance with high energy density and long cycle life thus would represent a major breakthrough in energy storage.

We synthesized metal oxide nanocrystals at a size of several nanometers on graphene, but found that rapid charging–discharging achieves only about 15% of their full capacitance. We hypothesized that reducing their sizes to the atomic clusters of subnanometer scales less than 1 nm, combined with conducting flexible graphene, would allow full redox reactions over entire constituents. Here we report that lithiation of 3-nm nickel oxide nanocrystals on graphene (NiO-n/gr) causes them to rescale down to subnanometer-scale Ni:Li$_2$O-a/gr core–shell clusters and that subsequent delithiation of Ni:Li$_2$O core–shell clusters leads to NiO (NiO-a/gr). We established the sequence as follows:

$$NiO\text{-}n/gr \rightarrow Ni:Li_2O\text{-}a/gr \rightarrow NiO\text{-}a/gr.$$
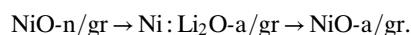
We then verified this using a combination of experimental characterization with complementary reactive molecular dynamics.

Moreover, we show that loading a positive electrode with NiO-a particles into an asymmetric full cell enables full capacitance of the counter negative electrode (15).

Results and Discussion

We prepared NiO-n/gr as described in *SI Appendix*, section S1. The structure and the composition of NiO-n/gr were determined using transmission electron microscopy (TEM) and powder X-ray diffraction (*SI Appendix*, Figs. S1 and S2) showing size of ~3 nm. Next, the sample was combined with PVDF as a binder in an *N*-methly-2- pyrrolidone (NMP) solution before the cell assembly. The cell was assembled with a 25-μm monolayer polypropylene membrane, followed by soaking in a 1 M LiPF$_6$ electrolyte solution with a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (*Materials and Methods* and *SI Appendix*, section S3).

To rescale the NiO-n (Fig. 1*A*), we configured a cell with a lithium metal counter/reference electrode and carried out a cyclic voltammetry experiment using a VSP potentiostat (Bio-Logic) at a scan rate of 0.1 mV s^{-1} (*SI Appendix*, Fig. S3). After the first cycle of lithiation and delithiation, we disassembled the cell and recovered NiO-a/gr and then washed the cell with acetone. Finally, we dried the NiO-a/gr in a vacuum oven. Next, we used dark-field scanning TEM (STEM) to demonstrate that this lithiation–delithiation process rescales NiO-n/gr to NiO-a/gr (Fig. 1 *B* and *C*).

Using ex situ TEM, we traced the morphology of a single 3-nm NiO evolving during the rescaling process (Fig. 1 *D* and *E* and

Fig. 1. Process of lithiation-induced rescaling. (*A*) Schematic showing the lithiation rescaling process of nickel oxide nanoparticles from several nanometers to angstroms. (*B* and *C*) STEM images of pristine 3-nm NiO nanoparticles on graphene and rescaled NiO particles on graphene. (*D* and *E*) The proposed mechanism of surface Faradaic redox reactions on various particles and TEM images of NiO particles before and after lithiation-induced rescaling.

SI Appendix, Figs. S4 and S5). We took the same position on the grid at each stage before and after electrochemical cycling. The TEM images (Fig. 1*D*, *Inset*) show a single 3-nm NiO crystal with its lattice spacing and Fourier transformation pattern before rescaling. After rescaling, we could not detect a lattice or diffraction pattern (Fig. 1*E*). We also obtained STEM mapping images (*SI Appendix*, Fig. S5 *C* and *D*), where the bright-colored spots visualize NiO particles rescaled on graphene.

We evaluated energy storage characteristics of NiO-a/gr through galvanostatic testing in an aqueous electrolyte with hydroxide (OH$^-$) ions, as demonstrated schematically in Fig. 1 *D* and *E*. The NiO-a/gr exhibited high capacitance (2,231 F per $g_{total\ composite}$ within 0.5 V), being six times larger than the value (350 F) for NiO-n/gr. This shows that hydroxide ions can access the entire NiO constituents of NiO-a/gr through the reaction of

$$NiO + OH^- \rightleftarrows NiOOH + e^-.$$

We also found that lithiation followed by delithiation works on nanoparticles larger than 10 nm, as validated by ex situ TEM and STEM images of each individual particle. Whereas the 3-nm particles were rescaled to atom clusters, the 10-nm NiO nanoparticles were rescaled to 2–3-nm sizes (*SI Appendix*, Fig. S6). Moreover the 10-nm NiO particles were rescaled to roughly 2-nm particles at a slow rate of 6 d for charge and discharge, which could be sufficient for full lithiation of all of the particles (*SI Appendix*, Fig. S7). Furthermore, from ex situ STEM measurements after 1- and 20-cycle rescaling of 10-nm NiO particles on graphene (*SI Appendix*, Fig. S8), significant differences in the sizes of the rescaled particles were observed, even after 20 cycles. This supports the conclusion that the major rescaling of particles takes places during the first cycle and that the rescaled sizes after the initial cycle are well maintained, even after further processes for lithiation-induced rescaling. Ex situ X-ray diffraction measurements of the 10-nm NiO

on graphene before and after rescaling also support that rescaled NiO particles maintain their crystal structure (*SI Appendix*, Fig. S9). Both X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) spectra (*SI Appendix*, Figs. S10 and S11) provide evidence of NiO bonds with graphene. The O1s XPS spectra and the FTIR spectra for the oxygen-containing groups demonstrate that C–O–Ni linkages (16) between NiO and the graphene increased after rescaling. However, Raman spectroscopy indicates that the distortion of the graphene planes and the defects in graphene remained largely unaffected after rescaling (*SI Appendix*, Fig. S12). Moreover, the N$_2$ adsorption–desorption isotherms (*SI Appendix*, Fig. S13) show high surface area of 335 m^2 g^{-1} for rescaled particles. We also found that a similar process rescales cobalt oxide nanocrystals to subnanometer-scale particles (*SI Appendix*, Fig. S14).

To investigate the rescaling mechanism underlying these surprising experimental results, we carried out reactive force-field (ReaxFF) molecular dynamics (RMD) simulations. The ReaxFF parameters for Ni–Li–O–C in *SI Appendix*, Table S1 were optimized by fitting density functional theory calculations of various Ni–O and Li–O systems. We started with three models of NiO on the top of a graphene: a monolayer model, a semisphere (cap) model, and a sphere model (*SI Appendix*, Fig. S15) to find the most plausible morphology for the NiO nanoparticles on graphene. Our simulations at constant number, volume, and temperature (NVT) conditions (*SI Appendix*, Fig. S16) show that the cap model partially wetting the graphene is the most stable on graphene, consistent with experimental observations (*SI Appendix*, Figs. S1 and S2).

Atomic layers of Li atoms were periodically deposited multiple times onto the surface of the NiO cap model to simulate the lithiation process. In the first round (Fig. 2*A*), 191 Li atoms were added to saturate all available oxygen sites (one Li atom for each surface oxygen site). A 40-ps RMD simulation was carried out under an external electronic field of 0.03 V nm^{-1}. For the newly added Li atoms, a much stronger electronic field (3 V nm^{-1}) was applied to accelerate the diffusion of Li atoms into the NiO cap. After the 40-ps RMD simulation, we found that the NiO cap had expanded and flattened due to the addition of Li (Fig. 2*B*). More Li atoms are consequently added to more O sites and the RMD simulation was repeated using the same protocol every 40 ps. After three rounds of Li addition (Fig. 2 *A–D*), a total of 848 Li atoms had been added to the system, which achieved the target of a Li:O ratio of 2:1 reached in the experiments.

The simulation was then extended to 2 ns and the electronic field applied was reduced to 0.03 V nm^{-1} for all of the atoms. During this 2-ns simulation, the cap structures gradually broke apart, finally breaking into 26 pieces (Fig. 2 *E–G*): 11 pieces had fewer than 20 atoms; 9 pieces had between 20 and 40 atoms, whereas 6 pieces had more than 40 atoms, and the largest had 140 atoms. This size distribution is consistent with experimental STEM images (*SI Appendix*, Fig. S5). The detailed atomic structures from lithiation (Fig. 2*H*) lead to shell compositions of NiO$_3$Li$_6$, Ni$_6$O$_7$Li$_{12}$, Ni$_8$O$_7$Li$_{14}$, and Ni$_9$O$_8$Li$_{16}$ surrounding a core of metallic Ni^0 atoms. We thus found a Ni^0 core surrounded with a shell of OLi$_x$ ($x = 1.82$, slightly less than 2). As the Li atoms are added during lithiation, nanoparticles become positively charged and form a positively charged shell outside the core–shell structure. This helps to separate the clusters while preventing coalescence of the clusters. Delithiation simulations were carried out by removing all of the Li in Li$_2$O and OLi$_3^+$ molecules. This led to extra oxygen atoms being introduced around the oxygen-deficient NiO clusters. We carried out a 200-ps RMD simulation, and obtained the snapshots presented in Fig. 2 *K* and *L*. We found that oxygen reoxidized the Ni/gr to form NiO-a/gr. After removing Li, the oxygen atoms previously interacting with Li start oxidizing Ni^0 to Ni^{2+} via the formation of NiO clusters. Fig. 2 shows the atomic structures of these NiO clusters.

The RMD simulations showed that the state of Ni evolved from Ni^{2+} to Ni^0 and back from Ni^0 to Ni^{2+}. *SI Appendix*, Fig. S19 shows

Fig. 2. ReaxFF molecular dynamics simulation of rescaling a 3-nm NiO nanoparticle during lithiation and delithiation at 298 K. (*A*) The simulation started from an equilibrated NiO semisphere placed on graphene with the addition of Li (23%) to all available surface O sites (view from top and side). A 40-ps NVT simulation was carried out with an external electronic field of 0.03 V nm^{-1}. The newly added Li experienced an additional 3-V nm^{-1} electronic field, which could accelerate the diffusion of Li. (*B*) The obtained structure after the 40-ps MD simulation. More Li atoms (49%) were then added to the newly created surface O sites, and the same simulations were repeated for another two rounds. (*C* and *D*) The structures after an NVT simulation of these second and third round Li additions, respectively, where 848 Li atoms (100%) were added into the system after three rounds of Li addition. (*E–G*) The simulation was then extended to 2 ns and snapshots during the simulation are shown. (*H*) The enlargement of a selected area of *G* (red slashed rectangle) is shown in which the Ni–O–Li core shell structure can be clearly observed. (*I–K*) After removing all of the Li, a 200-ps NVT simulation was carried out to investigate the delithiation process. Snapshots taken during the simulation are also shown. (*L*) An enlargement of a selected area of *K* (red slashed rectangle) in which O reoxidized the Ni to form NiO at a subnanosized scale. Atoms are distinguished by different colors: C in gray, Ni in blue, O in red, and Li in yellow.

the atomic charge distributions on Ni in NiO (cap), Ni after lithiation, and Ni after delithiation, where the charge distributions were described by a Gaussian distribution. After lithiation, the charge of Ni corresponding to Ni^{2+} decreases to zero, corresponding to Ni^0. After delithiation, the metallic Ni was reoxidized to Ni^{2+}.

The Ni–Ni and Ni–O radial distribution functions (RDFs) are shown in *SI Appendix*, Figs. S17 and S18, respectively, and *SI Appendix*, Table S2 summarizes the peak positions and coordination numbers, which are also consistent with the processes of Ni^{2+} to Ni^0 and back to Ni^{2+}. At the beginning of the lithiation simulation (NiO), the Ni–Ni RDFs have a strong peak at 3.075 Å corresponding to the nearest Ni–Ni distance in the NiO crystal (Ni^{2+}). After lithiation, the Ni–Ni RDF shifted to 2.675 Å, close to 2.44 Å for metallic Ni. This supports the conclusion that Ni changes from Ni^{2+} and Ni^0 during lithiation. The peak position returns to 2.975 Å, close to the Ni–Ni distance, indicating the process of Ni^0 to Ni^{2+} in delithiation, thus implying that the Ni becomes oxidized again upon delithiation. In addition the coordination number of Ni–O and Li–O shows that the number of oxygen molecules coordinated to Ni decreased from 3.2 to 1.2 during lithiation, whereas the number of oxygen molecules bonded to Li is 1.8. This indicates that during lithiation Li dragged the oxygen out of the NiO crystal, transferring electrons to Ni. After delithiation, the number of oxygens coordinated to Ni increased to 2.6, which is slightly smaller than 3.2. This is because the produced NiO clusters are smaller than the original NiO cap. This is also evidence for the formation of subnanometer-scale NiO clusters on graphene.

To experimentally characterize the mechanism for lithium-induced rescaling, we used XPS and spectroelectrochemical methods under ex situ and in situ. The cell configuration consisted of a Li metal counter/reference electrode and the NiO-n/gr deposited on Au-coated glass as a working electrode. *SI Appendix*, Fig. S20 shows that the Au film is not affected during Li charge–discharge. The cyclic voltammetry (CV) characteristics were obtained for NiO-n/gr at a high scanning rate of 1 mV s^{-1} (Fig. 3*A*). The lithiation resulted in characteristic peaks at about 0.5 V (vs. Li/Li$^+$) for the reaction of NiO + 2Li$^+$ + 2e$^-$ ⇌ Ni: Li$_2$O at the first discharge. Meanwhile, the peaks at around 1.3 and 2.3 V show that the reverse reaction occurred during delithiation. These peaks indicate the typical characteristics of CV trends for the NiO electrode (16, 17). Also, the graphene-based electrode showed voltage plateaus at around 0.8 V for the first discharge, consistent with the well-known reaction of the carbon surface with lithium to form solid electrolyte interface layers (13). The Ni 2*p* XPS spectra at XPS1 and XPS2 points (Fig. 3*A*) show that after the discharging (lithiation) process (Fig. 3*B*) the initial Ni^{2+} state shifted to a lower binding energy by 852.8 eV for 2*p*3/2 of a Ni^0 state (18). At the end of the cycle corresponding to the XPS3 point (Fig. 3*A*), the Ni 2*p* spectrum shifted back to higher binding energy, indicating that Ni^0 has returned to Ni^{2+}.

We also monitored the electrochemical rescaling process using in situ spectroelectrochemical UV/vis measurements (*SI Appendix*, section S10, Figs. S21 and S22). The points at which the optical spectra were recorded are indicated in Fig. 4*A* by colored circles. In the first stage of the rescaling process during lithiation,

Fig. 3. Characterization of the lithiation-induced rescaling process for NiO. (*A*) CV (scan rate = 1 mV s^{-1}) with measurement points indicated for ex situ and in situ spectroscopy. (*B*) XPS data for Ni 2p1/2 and 2p3/2 of initial, lithiated (discharged), and delithiated (charged) NiO on graphene. (*C*) In situ spectroelectrochemical UV/vis absorbance spectra during lithiation-induced rescaling. (*D*) UV absorbance spectra at different stages of lithiation-induced rescaling. UV/vis absorbance spectra during lithiation (*Bottom*) and delithiation (*Top*) processes were measured at the points marked on the CV data (*A*).

absorption due to the *d–d* transitions (19) characteristic of Ni^{2+} (near 550 nm) becomes weaker, which we attribute to the gradual elimination of the Ni^{2+} state of NiO in favor of the Ni^0 state (Fig. 3*C*). The UV transmission measured ex situ (Fig. 3*D*, *Bottom*) shows that the band gap absorption peak for NiO (370 nm) vanishes during this process. When the reverse reaction occurs during delithiation, the *d–d* transition peak and the band gap absorption peak for NiO are recovered (Fig. 3*C*). However, it is broadened and blue-shifted (Fig. 3*D*, *Top*). A similar blue shift in the UV absorption band of NiO particles was observed in the absence of graphene (*SI Appendix*, Fig. S23). The reaction of Ni with Li$^+$ is thus reversible, but the NiO morphology is dramatically changed: the NiO particles become smaller, as revealed by the blue-shifted band gap. These spectral changes support the evidence from TEM and STEM imaging that the electrochemical process transforms NiO-n/gr into NiO-a/gr.

The full capacitance of NiO-a/gr was also investigated in a three-electrode cell. To correlate the electrochemical performance with scalable NiO loading, we prepared three samples of NiO-n/gr with ~30 wt %, 50 wt %, and 70 wt % of NiO, respectively, denoted as NiO$_{30}$-n/gr, NiO$_{50}$-n/gr, and NiO$_{70}$-n/gr (*SI Appendix*, Fig. S24). The NiO content in each sample (*SI Appendix*, Fig. S25) was measured by a thermogravimetric analysis. We also assessed the electrochemical properties of NiO-g with CV measurements, where care was taken to establish an optimal and stable reference (*SI Appendix*, Fig. S26) and to remain within the stable voltage window of the electrolyte, determined using a blank Pt electrode (*SI Appendix*, Fig. S27). We initially established the capacitance contribution by the graphene, by measuring the CV of a NiO-free graphene electrode (*SI Appendix*, Fig. S28). For scan rates between 1 and 20 mV s^{-1}, the specific capacitance of the graphene ranged from 6.9 to 58 F per mass. Hence, the contribution of the graphene to the total capacitance of an optimized NiO-a/gr electrode (*SI Appendix*, Fig. S29) is less than 5%. The capacitance derives primarily from Faradaic redox reactions of NiO-n/gr or NiO-a/gr. This is associated with the pseudocapacitive behavior (20, 21) of

Faradaic oxidation and reduction peaks in the CV, consistent with the plateaus in the gravimetric charge–discharge curve (*SI Appendix*, Fig. S30). Moreover, the CV data at a scan rate of 5 mV s^{-1} before and after rescaling (Fig. 4 *A–C*) show that the intensity and the areas of both the cathodic and anodic peaks for NiO-a/gr dramatically increased. Among them, the capacitance of NiO$_{70}$-a/gr determined at a scan rate of 5 mV s^{-1} is 1,621 F g^{-1}, which is comparable with that from the gravimetric measurements. This enhancement is observed for each loading of NiO and for CV data measured at various scan rates (*SI Appendix*, Figs. S31*A*, S32*A*, and S33*A*).

To quantify the enhancement of capacitance after rescaling, we recorded the gravimetric charge–discharge behaviors of NiO-n/gr and NiO-a/gr in a potential window from 0 to 0.5 V (vs. Ag/AgCl), as shown in *SI Appendix*, Figs. S31*B*, S32*B*, and S33*B*. For a given current density, NiO-a/gr per mass showed capacitances that are several fold higher than those of NiO-n/gr (Fig. 4 *D–F*). High specific capacitances of 820, 1,533, and 2,231 F g^{-1} for NiO$_{30}$-a/gr, NiO$_{50}$-a/gr, and NiO$_{70}$-a/gr were obtained at 1.3, 1.3, and 1 A g^{-1}, respectively. It is notable that the capacitance of 3,023 F per the mass of pure NiO (g$_{NiO70-a}$), matching the measured capacitance of 2,231 F g$_{NiO70-a/gr}^{-1}$ considering the total mass of NiO$_{70}$-a/gr, exceeds the theoretical gravimetric capacitance of 2,618 F available via ion-to-atom redox reactions. This supports the conclusion that the lithiation rescaling makes it possible to obtain the ultimate capacity of the electrode by facilitating the redox reactions of active energy carriers to its entire constituents, in addition to additional contributions (22, 23) to the total capacitance. The capacitance of 2,231 F per the total electrode mass is

Fig. 4. Evaluation of the surface Faradaic reaction for lithiation-rescaled NiO. (*A–C*) CV data of (*A*) NiO$_{30}$-n/gr (black) and NiO$_{30}$-a/gr (red), (*B*) NiO$_{50}$-n/gr (black) and NiO$_{50}$-a/gr (blue), and (*C*) NiO$_{70}$-n/gr (black) and NiO$_{70}$-a/gr (green). (*D–F*) Gravimetric capacitances for various current densities on (*D*) NiO$_{30}$-n/gr (black) and NiO$_{30}$-a/gr (red), (*E*) NiO$_{50}$-n/gr (black) and NiO$_{50}$-a/gr (blue), and (*F*) NiO$_{70}$-n/gr (black) and NiO$_{70}$-a/gr (green). (*G*) Comparison of specific capacitance of NiO-n/gr and NiO-a/gr. (*H*) Charging–discharging cycle test of the lithiation-rescaled NiO on graphene up to 140,000 cycles.

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Fig. 5. Electrochemical properties of the asymmetric full-cell device. (*A*) Photograph of a coin-cell–type asymmetric supercapacitor that can store electrical energy to light up an LED. (*Inset*) Schematic cell configuration of the asymmetric full-cell device using NiO-a/gr and NG electrodes. (*B*) CV measurements of a two-electrode asymmetric full-cell device at various scan rates. (*C*) Charge–discharge profiles measured by galvanostatic characterization at various current densities. (*D*) Gravimetric capacitance of the full-cell configuration based on NiO-a/gr and NG electrodes in addition to that using NiO-a/gr and AC electrodes. (*E*) Cycling performance of asymmetric full-cell devices based on NiO-a/gr and NG electrodes in addition to that using NiO-a/gr and NG electrodes at a current density of 12 A g^{-1}. (*F*) Ragone plot of capacitors using NiO-a/gr and NG electrodes, NiO-a/gr and AC electrodes, and other data reported in the literature (31–37). All data in this figure are based on the asymmetric capacitor with the total mass of both electrodes.

extremely high compared with those in other morphologies such as NiO nanobelts (1,126 F g^{-1}) (24), porous NiO on carbon nanotubes (1,329 F g^{-1}) (25), and NiO/Ni nanocomposites (910 F g^{-1}) (26). Also, at high current densities of 33.3 and 35 A g^{-1} for NiO$_{30}$-a/gr, NiO$_{50}$-a/gr, and NiO$_{70}$-a/gr, the capacitances are 415, 690, and 1,670 F g^{-1}, respectively. These values are several times to several hundred times higher than those (2, 9, and 108 F g^{-1}) recorded for NiO$_{30}$-n/gr, NiO$_{50}$-n/gr, and NiO$_{70}$-n/gr, respectively. In all cases, the rescaling process dramatically enhanced the pseudocapacitive performance of NiO-n/gr (Fig. 4*G*). Moreover, the capacitance is maintained for cycling of NiO$_{50}$-a/gr at a current density of 20 A g^{-1} for over 100,000 cycles (Fig. 4*H*). The capacitances of NiO$_{30}$-a/gr and NiO$_{70}$-a/gr are similarly preserved during long cycle life (*SI Appendix*, Figs. S31*C* and S33*C*), thus implying that the rescaled particles do not suffer from degradation of the material over time (27, 28). This stability of NiO-a/gr was further validated using an alternative reference electrode (*SI Appendix*, Fig. S34).

A three-electrode cell was used to determine the available full capacitance for the electrode itself. Meanwhile, the practical device could be fabricated on a two-electrode full cell assembled using positive and negative electrodes. Our earlier report (15) showed that nitrogen-doped graphene is one of the best negative electrodes. In this view, we first fabricated an asymmetric supercapacitor full cell by combining nitrogen-doped graphene

(NG) as a negative electrode while using NiO-a/gr as a positive electrode. We find that this full cell provides sufficient power for operating an LED light (Fig. 5*A*) and it was operated in a voltage window of 1.6 V (Fig. 5*B*), which was determined through galvanostatic and CV measurements of NG (*SI Appendix*, Fig. S35) and NiO-a/gr. Fig. 5*C* shows that the full cell operates at a wide range of current densities (1.2–28 A g^{-1}). The highest capacitance we observed for the full cell is 223 F per g$_{NiO-a/gr||NG}$ at 1.2 A g^{-1} (Fig. 5*D*), where g$_{NiO-a/gr||NG}$ refers to the total mass of negative and positive electrodes. It is notable that the performance of this full cell is limited (29) by the negative electrode with a smaller capacitance of 285 F g$_{NG}^{-1}$ (*SI Appendix*, Fig. S35). Moreover, we also fabricated an asymmetric full cell using commercial activated carbon (AC) and NiO-a/gr as negative and positive electrodes, respectively (Fig. 5*D* and *SI Appendix*, Fig. S36). A capacitance of 118 F g$_{NiO-a/gr||AC}^{-1}$ at 1.5 A g^{-1}, close to the ultimate capacitance of AC (122 F g^{-1}), was obtained. Both full-cell devices present excellent stability with almost 100% capacity retention over 100,000 cycles at a fast current density of 12 A g^{-1}, compared with short cycle life using other metal oxide capacitors (30–32). These results suggest that the high-performance pseudocapacitive properties of the NiO-a/gr electrode would allow high capacitance and stable charge retention in a full-cell configuration with other promising counter electrodes.

Moreover, for the full cell using NiO-a/gr and NG electrodes, the highest energy density, ∼80 Wh kg^{-1} at a power density of about 1,000 W kg^{-1}, is achieved while it has the highest power density of ∼21,000 W kg^{-1} at an energy density of about 33 Wh kg^{-1} (Fig. 5*F* and *SI Appendix*, section S13). These energy and power densities are excellent compared with those of nickel-oxide–based capacitors (31, 32), nickel-hydroxide–based capacitors (33–35), and manganese-oxide–based asymmetric capacitor devices (36, 37).

Materials and Methods

Materials. All reagents unless otherwise stated were obtained from commercial sources (Sigma-Aldrich and Merck) and were used without purification.

Lithiation-Induced Rescaling. First, nickel oxide nanocrystals on graphene were prepared by nickel acetate and graphene oxide (38), as described in *SI Appendix*, section S1. To synthesize extremely small particles, we used a coin-type cell with Li metal as the counter electrode and with 1 M LiPF$_6$ dissolved in a mixture of EC and DEC as the electrolyte (1/1 = vol/vol) for the lithiation–delithiation. NiO on graphene was prepared as a working electrode by mixing with 10 wt % PVDF dispersed in NMP. The black slurry was coated on Cu foil and dried in a vacuum oven at 80 °C overnight. The test cells were assembled with a separator (Celgard) and an electrolyte solution in an Ar-filled glove box. The lithiation-induced rescaling of metal oxides was monitored by a VSP potentiostat (Bio-logic) at a scan rate of 0.1 mV s^{-1}. After these processes, the resulting samples were washed with acetone and water to remove residual electrolytes and lithium ions. We then measured the gravimetric mass of the rescaled NiO particles using thermogravimetric and inductively coupled plasma-optical emission spectroscopy analyses.

Modeling and Simulation. We started with metallic Li to directly simulate the reaction of NiO + 2Li$^+$ + 2e$^-$ ⇌ Ni:Li$_2$O. The ReaxFF used in this work combines the Ni–C–H–O force field (39) and Li–C–H–O force field (40) and was optimized to reproduce the conformational energies of Li–O finite molecules and Ni–O finite molecules. We started with a NiO cap on graphene, as shown in *SI Appendix*, Fig. S13*B*, for the pure NiO simulations and this same NiO cap with Li atoms added on top, as shown in Fig. 2*A*, for the lithiation simulations. Three rounds of Li addition were carried out to add a total of 848 Li atoms, and each addition was followed by a 40-ps NVT simulation under an external electronic field of 0.03 V nm^{-1} (3 V nm^{-1} for the newly added Li). The NVT molecular dynamics simulation was then extended to 2 ns to complete the lithiation. For delithiation, we carried out 200-ps NVT simulations after removing all of the Li atoms. A time step of 0.25 fs was used for all of the simulations. Nosé-Hoover temperature control was used in the NVT simulation at 300 K with a damping constant of 25 fs.

Measurement of Surface Faradaic Reactions. The capacitive performance was measured with a three-electrode device consisting of a platinum wire, a Ag/AgCl electrode (including SCE), and rescaled NiO on graphene, as the counter,

reference, and working electrodes, respectively. The working electrode was prepared by uniformly spreading a slurry composed of the lithiation rescaled sample and a binder (9:1 in mass) on nickel foil and by drying the sample in a vacuum oven at 80 °C. The electrochemical system was assembled with a 1 M KOH aqueous electrolyte and was sealed with Parafilm. The measurements were performed using a Bio-logic VSP potentiostat. The total mass of the composite in the electrode was between 1.3 and 1.5 mg cm^{-2}, measured using an XP2U ultramicrobalance (d = 0.1 μg, Mettler Toledo).

Full-Cell Type Asymmetric Supercapacitors. NG electrodes were prepared using the same method as reported in our previous study (15). To investigate the properties of a negative electrode, the as-obtained NG and AC for the negative electrode in a full-cell device were measured under a three-electrode cell configuration of a platinum wire, and a Ag/AgCl electrode in a 1 M KOH.

The CV and galvanostatic measurements were performed using the Bio-Logic VSP potentiostat. The electrochemical properties of the asymmetric full-cell device were investigated under a two-electrode cell configuration. The data analysis of the full-cell device is performed based on the total mass of samples for both electrodes (see *SI Appendix*, section S12 for details).

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