# LiCl/PVA Gel Electrolyte Stabilizes Vanadium Oxide Nanowire Electrodes for Pseudocapacitors

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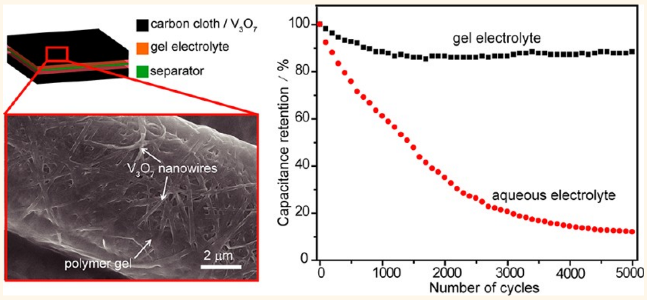
**ABSTRACT** Here we report a new strategy to improve the electrochemical stability of vanadium oxide electrodes for pseudocapacitors. Vanadium oxides are known to suffer from severe capacitance loss during charging/discharging cycling, due to chemical dissolution and ion intercalation/deintercalation-induced material pulverization. We demonstrate that these two issues can be addressed by using a neutral pH LiCl/PVA gel electrolyte. The function of the gel electrolyte is twofold: (i) it reduces the chemical dissolution of amphoteric vanadium oxides by minimizing water content and providing a neutral pH medium and (ii) it serves as a matrix to maintain the vanadium oxide nanowire network structure. Vanadium oxide nanowire pseudocapacitors with gel electrolyte exhibit excellent capacitance retention rates of more than 85% after cycling for 5000 cycles, without sacrificing the electrochemical performance of vanadium oxides.



**KEYWORDS:** vanadium oxides · LiCl/PVA gel electrolyte · nanowires · electrochemical stability · pseudocapacitors

Electrochemical supercapacitors are promising energy storage devices that can deliver higher power density than rechargeable batteries and higher energy density than conventional capacitors.[1,2] On the basis of their charge storage mechanism, supercapacitors can be classified into electrical double layer capacitors, where charges are physically separated, and pseudocapacitors, where charges are stored chemically through Faradaic reactions.[3−8] Pseudocapacitors with high specific capacitance hold great promise for practical applications. Conducting polymers (*e.g.*, polyaniline and polypyrrole)[9,10] and metal oxides (*e.g.*, $MnO_2$, NiO, and $RuO_2$)[7,8,11−14] have been extensively studied as electrode materials for pseudocapacitors. Among them, ruthenium oxides have been widely recognized as the best electrode material due to their extremely high specific capacitances (theoretical value 1358 F/g) and excellent cycling performance.[15] However, the scarcity (1 part per billion by weight in earth's crust) and extremely high cost (\$14 000 per kg) of ruthenium source limit its practical application as electrode material. In comparison to ruthenium oxide, vanadium oxides are earth-abundant materials and are inexpensive ($\sim$\$12 per kg). More importantly, vanadium has multiple stable oxidation states (II−V) and a smaller equivalent molecular weight than ruthenium, which allows it to have an even higher charge storage capability than ruthenium oxides.[14,16] Recently, vanadium oxides have been extensively studied as electrode materials for developing energy storage devices such as batteries[17,18] and pseudocapacitors.[14,16,19−24] However, severe capacity loss during charging/discharging cycling has been a major hurdle for developing vanadium-based pseudocapacitors and batteries.[18,21,25−28] The electrochemical instability of vanadium oxides is mainly attributed to the dissolution of electrode material and poor structural stability during charging/discharging cycling.[18,21,24,29] First, vanadium(V) oxide forms soluble species such as $H_2VO_4^-$ or $HVO_4^{2-}$ in aqueous solution. Intermediate species such as vanadium(III)

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oxide generated during the charging/discharging process also form soluble vanadate ions in water.[30] Second, vanadium oxides are amphoteric materials, which dissolve in both basic and acidic solutions. Third, the repeated ion intercalation/deintercalation process severely damages the morphology and crystal structure of vanadium oxides. As a result of structural breakdown, the crystalline vanadium oxide becomes amorphous nanoparticles that are loosely connected, thus causing substantial loss of capacity.[21] Various methods have been reported to address these problems. For example, an organic electrolyte has been used for vanadium oxide based lithium ion batteries to prevent the dissolution of the vanadium oxide electrode.[28] However, this method was not able to address the structure pulverization during lithium ion intercalation/deintercalation.[31] Liu *et al*. recently demonstrated that deposition of a layer of $Al_2O_3$ on vanadium oxide can strengthen its mechanical stability.[21] They observed that the capacitance of vanadium oxide was stable in an organic electrolyte for 50 charging/discharging cycles; however, long-term cycling performance was not reported. In addition, the insulating $Al_2O_3$ coating could increase the electrode resistance and affect the intercalation/deintercalation of lithium ions. Here we demonstrate a new strategy to stabilize the electrochemical performance of vanadium oxide using a gel electrolyte. In addition to being an ion diffusion matrix, the LiCl/PVA gel electrolyte can prevent the chemical dissolution of vanadium oxides by minimizing the water content and provide a neutral pH medium, as well as serve as an elastic coating to avoid structure pulverization by enhancing the mechanical strength of vanadium oxides.

This work is focused on improving the electrochemical stability of vanadium oxide nanowire electrodes for pseudocapacitors. Low-dimensional structures such as nanowires provide large surface areas for ion absorption/desorption from electrolytes into electrode materials, which could consequently lead to improved capacitance and rate capability.[6,7,27] Yet, the increased interfacial area between nanostructured vanadium oxides and an aqueous electrolyte could also increase the rate of chemical dissolution and structure pulverization, compared to the bulk structure. This work constitutes the first example of gel electrolyte stabilized vanadium oxide electrodes that have more than 85% capacitance retention rate after 5000 charging/discharging cycles. The success of stabilizing vanadium oxides in a LiCl/PVA gel electrolyte offers new opportunities in the design and fabrication of high-performance energy storage devices including pseudocapacitors and lithium ion batteries.

## RESULTS AND DISCUSSION

Vanadium oxide nanowires were synthesized on flexible conducting carbon cloth substrates using a hydrothermal method (see the Experimental Section). Scanning electron microscopy (SEM) images show that the as-prepared nanowires are uniformly self-assembled on each carbon fiber (Figure 1a), and more importantly, the nanowires form a network structure that connects all the carbon fibers (Figure 1b). Transmission electron microscopy (TEM) studies reveal that the diameters of these nanowires are around 100 nm (Figure 1c and Figure S1a and b, Supporting Information). The electron diffraction (Figure 1c, inset) and lattice-resolved TEM image (Figure S1c, Supporting Information) confirm that the vanadium oxide nanowires are single crystals. To identify the chemical composition and crystal structure of as-prepared vanadium oxide nanowires, we performed X-ray diffraction (XRD) measurements on nanowire powders. The X-ray diffraction peaks of the nanowires can be indexed as orthorhombic $V_3O_7 \cdot H_2O$ (PCPDF no.: 28-1433) and monoclinic $V_3O_7$ (PCPDF no.: 27-0940) (Figure 1d). Furthermore, an X-ray photoelectron spectroscopy (XPS) survey spectrum collected from a vanadium oxide film confirms the presence of V and O (Figure S2, Supporting Information), without other impurities. The carbon signal is due to the carbon cloth substrate. Figure 1e shows the core level V 2p XPS spectrum of a vanadium oxide film. Note that the V $2p_{3/2}$ has a broad peak with a shoulder at 516.4 eV, indicating the presence of mixed valence states of vanadium. The V $2p_{3/2}$ peak was deconvoluted into two synthetic peaks. The deconvoluted V $2p_{3/2}$ binding energies of 517.7 and 516.4 eV are consistent with typical values reported for $V^{5+}$ (*ca*. 517.1 to 517.7 eV)[32,33] and $V^{4+}$ (*ca*. 516 to 516.6 eV).[34] The ratio of $V^{4+}$ to $V^{5+}$ is close to 1:2, as expected for $V_3O_7$. On the whole, these results support the successful preparation of a $V_3O_7$ nanowire network on carbon cloth.

We fabricated symmetrical pseudocapacitors based on a vanadium oxide nanowire network on carbon cloth and investigated their electrochemical performance in a 5 M LiCl aqueous solution and a LiCl/PVA gel electrolyte (Experimental Section). Gel electrolytes have been demonstrated as a replacement of aqueous electrolytes for solid-state pseudocapacitors. However, common gel electrolytes such as PVA-$H_2SO_4$, PVA-$H_3PO_4$, and PVA-KOH cannot be used for vanadium oxides, as they are amphoteric materials that can dissolve in basic or acidic medium (Figure S3, Supporting Information). It has been a challenge to develop a neutral gel electrolyte because common metal salts such as $Na_2SO_4$, NaCl, and KCl would be easily crystallized out during the gel preparation. Significantly, we found that LiCl can be well dissolved in PVA gel without crystallization during the gel drying process. The gel maintains excellent electrochemical and mechanical properties without the need to be wetted periodically (Figure S4, Supporting Information). Figure 2a shows the cyclic voltammograms of vanadium oxide pseudocapacitors with a gel electrolyte

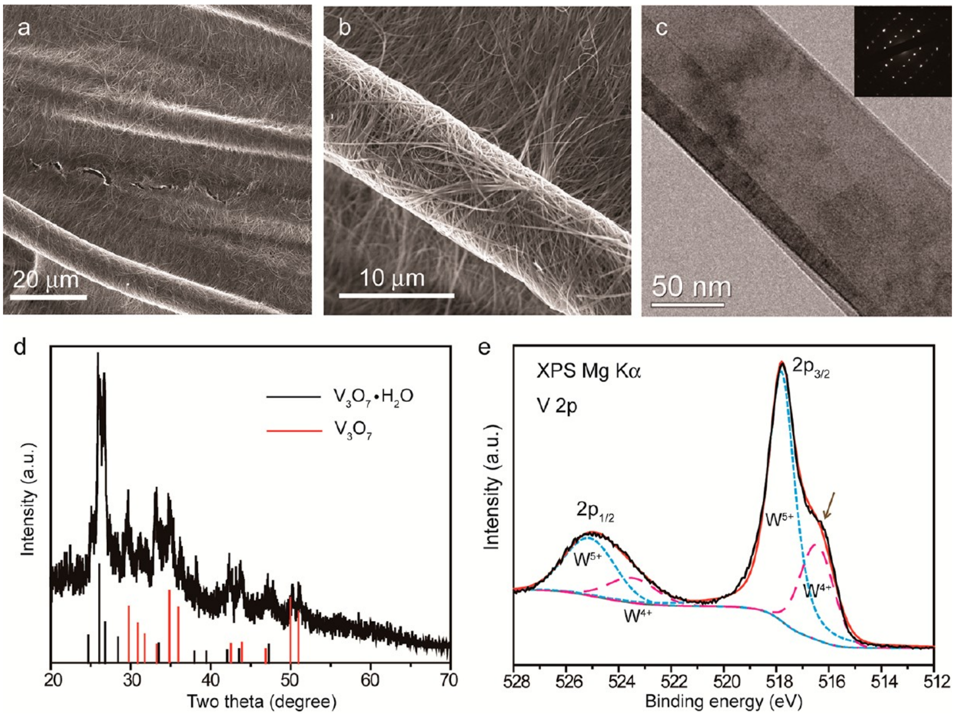

**Figure 1. (a) SEM image of as-prepared vanadium oxide nanowire networks on a carbon cloth. Scale bar is 20 μm. (b) Magnified SEM image showing a single carbon fiber is completely coated with vanadium oxide nanowires. Scale bar is 10 μm. (c) TEM image of a vanadium oxide nanowire. Scale bar is 50 nm. Inset: Electron diffraction pattern. (d) XRD spectrum collected for vanadium oxide nanowire powder. The red and black lines at the bottom indicate the diffraction peaks of orthorhombic $V_3O_7 \cdot H_2O$ (PCPDF no. 28-1433) and monoclinic $V_3O_7$ (PCPDF no. 27-0940). (e) V 2p XPS spectrum collected for vanadium oxide nanowires. The black curve is the experimental result. The red curve is the summation of the fitting curves (dashed curves).**

collected at scan rates of 5, 10, and 20 mV/s using a two-electrode system. As expected, the current density increases with the scan rates. The redox couple is an indication of superior reversible Faradaic reactions on the electrode surface. The Faradaic reaction is believed to be due to the absorption of ions such as lithium ions and protons,[35] which has been observed in LiCl and $LiClO_4$ solution.[19−21] The same set of redox peaks was also observed in the cyclic voltammogram collected for vanadium oxide pseudocapacitors in a LiCl aqueous solution (Figure S5a, Supporting Information). Note that the redox peak intensities and, thus, the pseudocapacitance of vanadium oxide obtained in a gel electrolyte are substantially higher than those obtained in aqueous solution. The enhanced pseudocapacitance could be due to higher lithium ion concentration in the gel electrolyte, which facilitates lithium ion diffusion and absorption. Galvanostatic charging/discharging profiles collected in gel and aqueous electrolytes at current densities in the range between 0.2 and 6.0 mA/cm$^2$ are shown in Figures 2b and S5b (Supporting Information), respectively. The nonlinear charging/discharging profiles indicate a significant contribution of pseudocapacitance from vanadium oxides. The relatively large *IR* drop could be due to the high resistance of vanadium oxides.[19] Figure 2c shows the calculated areal capacitances of vanadium oxides after *IR* drop compensation at different charging/discharging current densities. Importantly, the areal capacitance of a vanadium oxide pseudocapacitor in a gel electrolyte is higher than that in aqueous solution at all current densities studied. It achieves a maximum areal capacitance of 236 mF/cm$^2$ in gel electrolyte at a charging/discharging current density of 0.2 mA/cm$^2$. The loading amount of electrochemically active vanadium oxide on each electrode was measured to be 0.9 mg/cm$^2$, and therefore the specific capacitance for the whole pseudocapacitor is calculated to be 131 F/g. The vanadium oxide pseudocapacitors retain 68% and 85% of their initial capacitances in the LiCl gel and aqueous electrolyte, respectively, when the charging/discharging current density increased from 0.2 to 6.0 mA/cm$^2$. The relatively higher capacitance retention in aqueous solution can be attributed to better ion diffusion. The capacitance retention (85%) in LiCl aqueous solution is comparable to the values reported for vanadium oxides coated on carbon nanotubes by atomic layer deposition.[19] The Coulombic efficiencies of vanadium oxide in the gel electrolyte in the entire range of charging/discharging current densities between 0.2 and 6 mA/cm$^2$ are higher than 92%. All these results prove that vanadium oxide pseudocapacitors exhibit excellent electrochemical properties in a gel electrolyte.

To prove our hypothesis that a gel electrolyte can increase the mechanical stability and minimize the chemical dissolution of vanadium oxides, we further tested the cycling performance of vanadium oxide

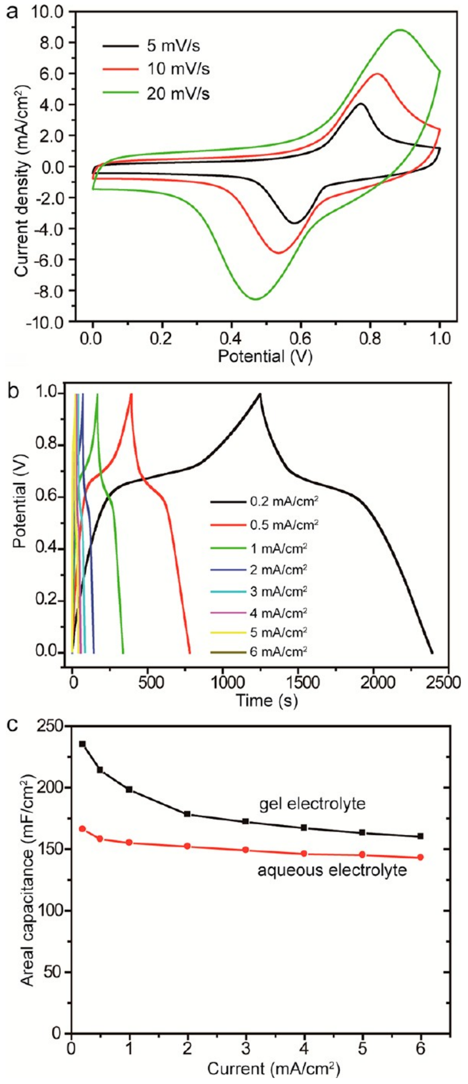

**Figure 2. (a) Cyclic voltammograms collected for a vanadium oxide pseudocapacitor in a LiCl/PVA gel electrolyte at scan rates of 5, 10, and 20 mV/s using a two-electrode system. (b) Galvanostatic charging/discharging profile of a vanadium oxide pseudocapacitor measured in the gel electrolyte at current densities in a range between 0.2 and 6 mA/cm$^2$. (c) Calculated areal capacitance of vanadium oxide pseudocapacitors in the LiCl/PVA gel and 5 M LiCl aqueous electrolyte (after compensation of *IR* drops) measured at current densities in a range between 0.2 and 6 mA/cm$^2$.**

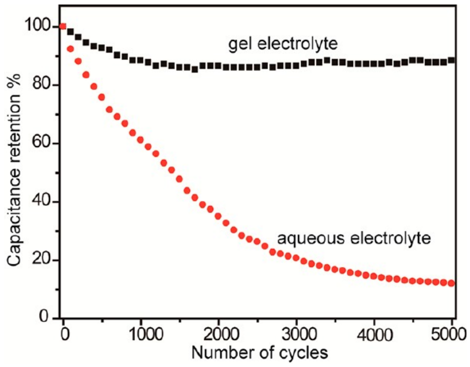

**Figure 3. Comparison of cycling performance of vanadium oxide pseudocapacitors in a 5 M LiCl aqueous electrolyte and a LiCl/PVA gel electrolyte. The capacitance was calculated on the basis of the CV scans collected at a scan rate of 100 mV/s.**

pseudocapacitors in a gel electrolyte and compared it to the values obtained in an aqueous electrolyte. As shown in Figure 3, the capacitance of vanadium oxides decreases continuously in aqueous solution. After 5000 cycles, only 10% of the initial capacitance was retained. In contrast, the capacitance decreases slowly in the gel electrolyte for the first 1000 cycles and then remains stable for further cycling. Significantly, more than 85% of the initial capacitance was retained after 5000 cycles. This work constitutes the first example of a vanadium oxide electrode that can be stabilized at least for 5000 cycles, and more importantly, the gel electrolyte stabilizes the vanadium oxide electrodes without sacrificing their electrochemical performances.

We performed SEM studies on the vanadium oxide electrodes during the cycling test to elucidate the correlation between the electrochemical stability and the structure changes of vanadium oxide during repeated cycling in aqueous and gel electrolytes. Figure 4 shows the SEM images collected for vanadium oxide electrodes that were tested in the LiCl aqueous solution during the first 3000 cycles. As shown in Figure 4a and b, the nanowire network structure begins breaking down into nanowire segments after cycling for the first 200 cycles, although each carbon fiber is still uniformly covered with the nanowires. At 1000 cycles, the nanowire structure starts to fuse into a dense film. The collapse of the nanowire structure could be due to the continuous volume expansion and shrinking during the cycling test as a result of lithium ion absorption/desorption. This has been observed in silicon nanowire based electrodes for lithium ion batteries.[36] After 3000 cycles, all nanowires disappear, and the carbon fiber appears to be coated with a densely packed particle film. Additionally, the aqueous electrolyte became a light yellow solution (Figure S5c, Supporting Information) after 3000 cycles. Vanadate ions (yellow in color) were detected in the yellow solution by inductively coupled plasma atomic emission spectroscopy, indicating the chemical dissolution of the vanadium oxide nanowires. These results confirmed that the poor cycling performance of vanadium oxides in aqueous solution is related to the undesirable chemical dissolution and the nanowire structure pulverization.

Furthermore, the solid-state pseudocapacitor devices with gel electrolyte were disassembled for SEM analysis by slowly dissolving PVA gel in ethanol. SEM images collected for the vanadium oxide electrodes after testing for 5000 cycles in gel electrolyte are displayed in Figure 5. Figure 5a shows that the carbon fibers were uniformly wrapped by the polymer gel. After dissolving a portion of the polymer gel, the SEM images reveal that the vanadium oxide nanowire network structure remains unchanged after cycling

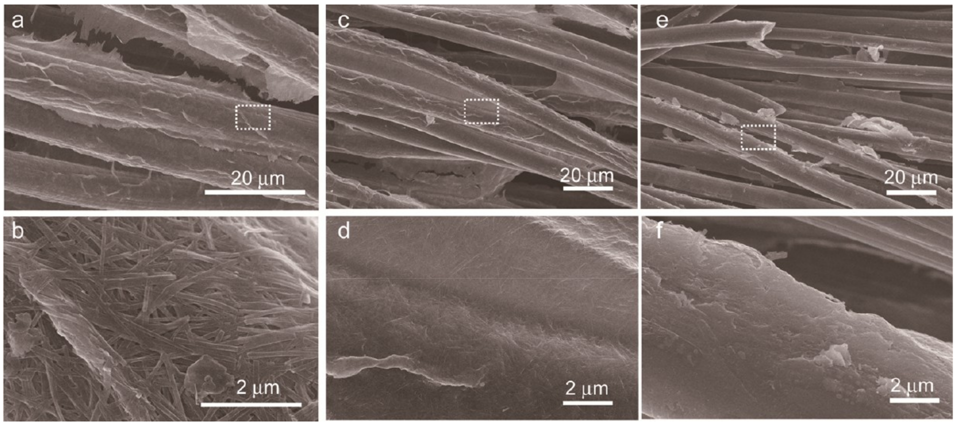

**Figure 4.** SEM images collected for vanadium oxide electrodes after cycling for (a, b) 200 cycles; (c, d) 1000 cycles; and (e, f) 3000 cycles. (b, d, f) Magnified SEM images in the dashed boxes in a, c, and e, respectively.

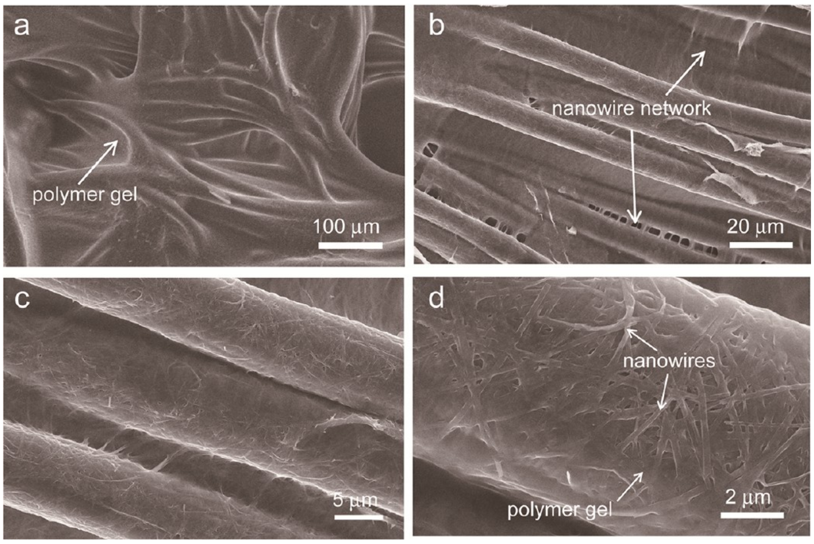

**Figure 5.** (a) SEM image of vanadium oxide nanowire coated carbon cloth wrapped by LiCl/PVA polymer gel. (b–d) SEM images of vanadium oxide nanowire electrode after testing for 5000 cycles in the gel electrolyte.

(Figure 5b and d), indicating the gel electrolyte protects the vanadium oxide nanowires from chemical dissolution and structural pulverization. These results fully support our hypothesis that the polymer gel electrolyte not only serves as a neutral pH matrix for ion diffusion but also functions as an elastic shell to retain the nanowire structure during repeated ion absorption/desorption.

## CONCLUSION

In summary, our studies showed that the electrochemical instability of vanadium oxides is mainly due to chemical dissolution in aqueous electrolyte and structure pulverization during charging/discharging cycling. We have demonstrated a novel strategy to address these limitations by replacing the aqueous electrolyte with a neutral pH LiCl/PVA gel electrolyte. The vanadium oxide nanowire pseudocapacitors with gel electrolyte achieved a maximum areal capacitance of 236 mF/cm$^2$ at a current density of 0.2 mA/cm$^2$ and an excellent capacitance retention rate of more than 85% after cycling for 5000 cycles. This work presents the first demonstration of using a gel electrolyte in stabilizing vanadium oxide electrodes. The same strategy could be applied to other electrode materials used in pseudocapacitors or lithium ion batteries that suffer from electrochemical instability and, thus, could open up new opportunities in the design and fabrication of energy storage devices.

## EXPERIMENTAL SECTION

**Synthesis of Vanadium Oxide Nanowire Network.** A 0.162 g amount of $NH_4VO_3$ was dissolved in a 25 mL solution of water and ethanol (volume ratio: 9:1). The solution pH was adjusted to ~2 by HCl. The 25 mL solution was transferred to a 30 mL Teflon-lined autoclave. A piece of carbon cloth was cleaned by acetone, ethanol, and then water and immersed into the precursor solution in the autoclave. The sealed autoclave was heated in an electric oven at 160 °C for 12 h and then allowed to cool at room temperature. The carbon cloth was washed with distilled water and blown dry with compressed air. The carbon cloth was coated with a layer of greenish-blue film composed of nanowires.

**Preparation of LiCl/PVA Gel Electrolyte.** A 4 g sample of polyvinyl alcohol (PVA) powder was dissolved in 40 mL of distilled water at 95 °C with stirring. After the PVA powder was completely dissolved, 8.5 g of LiCl was added into the PVA solution under vigorous stirring until it formed a homogeneous sticky solution. The solution was cooled at room temperature, and the solution became a clear and transparent gel.

**Assembly of Pseudocapacitor Devices.** *Pseudocapacitors Used for Measurements in Aqueous Electrolyte.* A piece of filter paper was used as a separator. The filter paper was sandwiched between two pieces of vanadium oxide nanowire coated carbon cloth (1.0 cm × 1.0 cm) and then immersed into a 5 M LiCl aqueous solution.

*Solid-State Pseudocapacitors with Gel Electrolyte.* A piece of filter paper and two pieces of carbon cloth coated with vanadium oxide nanowires were immersed into the LiCl gel electrolyte for 3 min and then allowed to dry in air for 30 min. The filter paper was sandwiched between two pieces of carbon cloth (with an overlapped area of 1.0 cm × 1.0 cm). The assembled pseudocapacitor device was further dried at 40 °C in an electric oven for 12 h. The device was then sealed in parafilm foil with insulating epoxy to prevent the gel electrolyte from absorbing moisture.

**Material Characterization.** X-ray diffraction spectra were collected on a Rigaku Americas Miniflex Plus powder diffractometer. Scanning electron microscopy images were collected with a field emission SEM (Hitachi S-4800II). X-ray photoelectron spectroscopy was performed on an RBD upgraded PHI-5000C ESCA system (Perkin-Elmer) using Mg-monochromatic X-rays at a power of 25 W with an X-ray-beam diameter of 10 mm and a pass energy of 29.35 eV. The pressure of the analyzer chamber was maintained below $5 \times 10^{-8}$ Pa during the measurement. The binding energy was calibrated using the C 1s photoelectron peak at 284.6 eV as reference. Raman spectroscopy measurements were carried out on a Nicolet Almega XR Dispersive Raman spectrometer (laser wavelength 780 nm).

**Electrochemical Characterization.** The electrochemical properties of the samples were investigated by cyclic voltammetry (CV) and galvanostatic charge/discharge measurements in a two-electrode configuration using a CHI 660D electrochemical workstation. The cycling performance was tested by cyclic voltammetry sweeps at a scan rate of 100 mV/s for 5000 cycles.

*Conflict of Interest:* The authors declare no competing financial interest.

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*Supporting Information Available:* TEM images, XPS, digital picture of LiCl/PVA film, CV, and charging/discharging curves. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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