Accepted Article

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemElectroChem 10.1002/celc.201700102

Link to VoR: http://dx.doi.org/10.1002/celc.201700102
Reinvigorating Reverse Osmosis Membrane Technology to Stabilize V$_2$O$_5$ Lithium Ion Battery Cathode

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Abstract:

V$_2$O$_5$ is deemed as one of the most promising cathode materials for next generation high capacity LIBs. It possesses a theoretical capacity of 294 mAh g$^{-1}$ that is much higher than conventional cathodes. However, there are many issues to be solved before its practical use, including poor cycle life and unsatisfactory rate performance, mainly due to its low electronic conductivity and ionic diffusivity, as well as structural instability. This work reports three types of V$_2$O$_5$ asymmetric membranes synthesized using an adapted reverse osmosis membrane technology combined with sol-gel chemistry, aiming to stabilize the cyclability and improve the rate performance. V$_2$O$_5$ asymmetric membrane cathodes prepared using graphene as the conductive additives have a specific capacity of ~160 mAh g$^{-1}$ at a current density of 100 mA g$^{-1}$ with no capacity degradation after 380 cycles. It is also found that annealing temperature and the choice of conductive additives can affect the morphology of V$_2$O$_5$ nanoparticles and overall electrode cyclability. Lower annealing temperature (300 °C vs. 400 °C) and addition of graphene are beneficial to long term cycling performance.

Key Words:
Vanadium Pentoxide; Asymmetric Membrane; Phase Inversion; Sol-Gel; Lithium Ion Battery Cathode
1. Introduction

Lithium ion batteries (LIBs) have broad applications in mobile electronics, electric vehicles and large scale static energy storage. The conventional LIB cathode materials generally have capacities below 200 mAh g\(^{-1}\), which are much lower than that of graphite anode (372 mAh g\(^{-1}\)). \cite{1,2} Thereby it is highly important to explore alternative cathode materials that have comparable capacities as graphite to further improve the overall energy density of LIBs. V\(_2\)O\(_5\) as one of the most promising high capacity cathode materials for LIB possesses a theoretical capacity of 294 mAh g\(^{-1}\) when two lithium ions are intercalated into one V\(_2\)O\(_5\) unit.\cite{3,4} However, the cycle life and rate performance of V\(_2\)O\(_5\) cathode is not satisfactory because of its low electronic conductivity and ionic diffusivity, as well as structural instability.\cite{1,5} Recently, nanostructured V\(_2\)O\(_5\) materials have been investigated to circumvent these problems, including nanowires (NWs), nanobelts (NBs) and nanoparticles (NPs), which enable shorter electron transport and ion diffusion lengths, and thus overcomes its poor conductivity and diffusivity.\cite{6-14} When further mixing V\(_2\)O\(_5\) nanomaterials with conductive additives like graphene and conductive polymers, the rate performance of V\(_2\)O\(_5\) can be significantly improved due to the enhanced electron transfer efficiency. For instance, amorphous V\(_2\)O\(_5\) nanobelts/graphene composite demonstrated a high capacity up to 400 mAh g\(^{-1}\) for the first cycle, which maintained above 200 mAh g\(^{-1}\) after 200 cycles at a relatively slow charging/discharging rate.\cite{15} Graphene nanoribbon/V\(_2\)O\(_5\) nanoparticle composite showed an initial capacity of \(\sim\)250 mAh g\(^{-1}\) and retain nearly 80% capacity after 100
cycles.[3] Besides nanostructuring, another effective way to enhance the cyclability of V$_2$O$_5$-based cathode is to assemble V$_2$O$_5$ nanomaterials into a robust 3-D microstructure, which can efficiently prevent the agglomeration of nanomaterials after repeating lithiation and de-lithiation.[16]

Reverse osmosis membranes prepared using a phase inversion method are characteristic of a nanoporous skin layer and a macroporous bottom layer. Such a unique porous structure can provide free volume for electrode to expand and prohibit fractured active materials from being leaked out into electrolyte, thus benefiting structure integrity and long cycle life. Recently, this membrane technology has been reinvigorated by our laboratory to enhance the cyclability of high capacity LIB anodes that suffer from large volume changes.[17,18] In this report, the reverse osmosis membrane technology has been adapted to increase the stability of V$_2$O$_5$ LIB cathode. Two types of V$_2$O$_5$ asymmetric membranes have been prepared using a phase inversion method combined with sol-gel chemistry. As-prepared membranes containing polymers are treated at high temperatures to make them electrically conductive. These membranes are systematically characterized by using scanning electron microscope (SEM), high resolution electron microscope (HRTEM), energy dispersive spectroscopy (EDS), Raman spectroscopy, power X-ray diffractometer (PXRD), thermogravimetric analyzer (TGA), surface area analyzer (BET method) and X-ray photoelectron spectroscopy (XPS). The membranes are also evaluated as LIB cathodes that demonstrate a high capacity of 160 mAh g$^{-1}$ at C/2 with ~100% capacity
 retention after 380 cycles. The effects of treatment temperatures and conductive additives on their electrochemical properties are also investigated herein.

2. Experimental Section

2.1. Synthesis of $V_2O_5$ asymmetric membranes using a phase inversion method combined with sol-gel chemistry

First, 0.5 g polysulfone ($M_n \approx 60,000$, pellets, Acros) was dissolved in 5 mL N-methyl-2-pyrrolidone (NMP) (Sigma Aldrich, >99.5%) under sonication (Branson CPX3800H) followed by adding 0.1 g carbon black (CB, TIMCAL SUPER C45 with a surface area of 45 m$^2$ g$^{-1}$) or 0.1 g graphene (GH, cheaptube.com, >98 wt.%, 20-100 nm in diameter, >750 m$^2$/g) into the polymeric solution. Then 2.0 g vanadium (V) oxytriethoxide (VOTEO, 95%, Acros Organics) were mixed with the polymeric solution containing CB or GH by 15 min vortexing and 5 min sonication. The mixture was coated onto a glass plate using a doctor blade with a wet thickness of ~150 µm. The coated glass plate was immediately immersed into deionized water (~18 MΩ) for phase inversion. The as-formed asymmetric membrane separated from the glass substrate naturally after ~5 minutes. Finally, the asymmetric membrane was dried and treated at high temperatures using a Lindberg/Blue M™ 1100°C tube furnace with a ramp rate of ~60 °C min$^{-1}$. The membranes were treated at high temperatures via a two-step method: 1) the membranes were first carbonized at 500 °C for 1 hr under the protection of high purity helium gas (99.9999%, Airgas He UHP300) of 200 sccm flow rate to facilitate electrical conductivity while maintaining the porous structure and 2) the membranes
were then heated in air from room temperature to 400 °C in 5 minutes or heated in air at 300 °C for 1.5 hrs to retrieve vanadium (V) oxide. The asymmetric membrane prepared using CB and heated up to 400 °C in air in 5 minutes was labeled V$_2$O$_5$ EO-400 CB; the asymmetric membrane prepared using CB and heated at 300 °C in air for 1.5 hr was labeled as V$_2$O$_5$ EO-300 CB; and the asymmetric membrane prepared using graphene and heated at 300 °C in air for 1.5 hr was labeled V$_2$O$_5$ EO-300 GH. We also fabricated control asymmetric membrane without using CB or GH additives to test whether V$_2$O$_5$ alone is an efficient cathode component. The control membrane was carbonized and then heated at 300 °C in air for 1.5 hr, which was labeled as V$_2$O$_5$ EO-300 without CB or GH.

2.2. Characterization of V$_2$O$_5$ asymmetric membranes

A Field Emission Scanning Electron Microscopy (JEOL JSM-7600F) attached with Transmission Electron Detector (TED) was employed for membrane morphological and structural characterization. High Resolution Transmission Electron Microscopy (HRTEM) characterization was performed using a JEM 2100F TEM (JEOL Ltd., Japan) operated at accelerating voltages of 120 to 200 kV. A Thermo Scientific DXR SmartRaman Spectrometer was operated using a 532 nm laser of 5 mW, an objective lens of ×10, and a total integration time of 120 seconds. Powder X-ray diffraction (Scintag XGEN-4000) was taken using a Cu K$_\alpha$ radiation (λ=1.542 Å) from 10 to 70° (two theta) with a step rate of 0.1°/s. The acceleration voltage and current are 40 kV and 15 mA, respectively. V$_2$O$_5$ asymmetric membranes were also analyzed for their elemental composition and oxidation states using an X-ray photoelectron
spectroscopy (PHI 5000 Versaprobe XPS system from Physical Electronics, Inc.), which employed monochromatic Al Kα X-rays of energy 1486.6 eV. Powder samples were mounted onto the XPS sample holder using a double-sided carbon tape. An X-ray spot size of 200 mm at ~ 50 W was used for data acquisition. Survey scans at pass energy of 117 eV were performed for the chemical elemental identification. To determine the chemical bonding states, we acquired region spectra at pass energy of 23.5 eV. The takeoff angle was kept constant at 45°. The specific surface areas of four kinds of asymmetric membranes were measured using a Micromeritics ASAP 2020 Surface Area and Porosimetry Analyzer, which were calculated using Brunauer-Emmett-Teller (BET) method. Membrane samples were degassed at 50 µTorr and 300 °C for 30 minutes. The content of V₂O₅ was determined by a thermogravimetric analyzer (NETXSCH STA 449 F3) using compressed air as the purging gas (Ultra Zero, Airgas). The flow rate of the compressed air gas is 20 mL min⁻¹ and the temperature was ramped from 25 to 550 °C at a rate of 10 °C min⁻¹, and then hold at 550 °C for 15 minutes. Pure V₂O₅ micron-size particles (10 meshes, 99.6% min., Alfa Aesar) were used as a reference in Raman, PXRD, XPS and TGA analysis.

2.3. Electrochemical evaluation of asymmetric membranes as LIB Cathodes:

V₂O₅ electrodes were prepared by adhering the asymmetric membranes directly onto aluminum discs (15 mm in diameter and 18 µm thick from MTI Corporation) using a glue consisting of 0.1 g carbon black and 0.1 g polyvinylidene difluoride (PVDF, MTI Corporation) dispersed in 3 mL NMP. The uncalendered electrode was dried at 120 °C for at least 4 hrs to remove residual NMP and H₂O moisture. The final mass of
membrane materials per electrode is ~2 mg. The electrode was then assembled into 2032-type coin cells using lithium metal (EQ-Lib-LiC25, MTI Corporation) as the counter electrode and 60 µL 1 M LiPF$_6$ dissolved in ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) with a volume ratio of 1:1:1 (MTI Corporation) as the electrolyte. Inside the glove box (LCPW, LC Technology Solutions, INC.), oxygen and water concentrations were maintained below 1 ppm. The membrane separator is ethylene/polypropylene blend with pore sizes 20-30 nm (MTI Corporation). Galvanostatic cycling tests of LIB half-cells were conducted using a multi-channel Potentiostat/EIS (BIO-LOGIC VMP3) at room temperature. The voltage window is 2.00–3.60 V (vs. Li/Li$^+$). For both rate performance and cyclability test, the cells were charged and discharged with the same current density. The cells were subject to five formation cycles at 20 mA g$^{-1}$ before any subsequent tests. Current densities of 20, 40, 100 and 200 mA g$^{-1}$ were applied to test the cell rate performance. Long term cyclability test was performed at 100 mA g$^{-1}$. During the cyclic voltammetry measurements, the voltage was scanned from 2.00 to 3.60 V at a rate of 0.05 mV s$^{-1}$. Electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range of 0.1 Hz–1 MHz with AC amplitude of 10 mV.

3. Results and Discussion

3.1. Fabrication of V$_2$O$_5$ asymmetric membranes

V$_2$O$_5$ asymmetric membranes were prepared using an adapted phase inversion method that has been utilized to fabricate polymeric asymmetric membranes on a
large scale for water desalination and purification.[19,20] CB or GH powders were added to increase the electrical conductivity and support the membrane backbone during the following carbonization. The transmission electron microscope images of CB and GH are shown in S1. In the phase inversion process, the thin film consisting of NMP, PS, VOTEO and CB (or GH) was immersed into water (non-solvent) to generate two phases, polymer rich and polymer lean phases, resulting in the spontaneous formation of asymmetric porous structure. As-formed inorganic/polymeric membranes were then carbonized to make the membrane conductive. The carbonized membranes were annealed in air at various temperatures to obtain \( V_2O_5 \) asymmetric membranes. It is notable that the membrane annealed at higher temperature in air is more fragile than the one annealed at lower temperature, because more carbon material is lost during the higher temperature anneal. Figure 1a illustrates the overall membrane fabrication process. Noteworthy this method is highly scalable as evident by a piece of 6 in \( \times \) 2 in membrane shown in Figure 1b. Cross-sectional SEM image reveals the membrane contains nanopores on its top surface and macropores underneath the nanopores (Figure 1c).

3.2. Characterization of \( V_2O_5 \) asymmetric membranes

SEM images of \( V_2O_5 \) asymmetric membranes after being annealed in air clearly show that the top layer is nanoporous, whereas the bottom layer is macroporous. The thickness of \( V_2O_5 \) asymmetric membrane is about 140 \( \mu m \) when annealed at 300 °C for 1.5 hr in air, and it is reduced to 120 \( \mu m \) when annealed at higher
temperature 400 °C albeit shorter annealing period, 5 min (Figure 2). The reduced thickness is ascribed to higher shrinkage induced by more carbon removal at higher oxidation temperature, which is also confirmed by our TGA analysis. In comparison, V$_2$O$_5$ EO-300 GH membrane is much thinner than other two types of membranes (~70 µm). It may be due to the strong π-π interactions between graphene sheets, leading to a denser packing. SEM image in S2 confirms that the reference sample consists of micron size particles. As revealed by the HRTEM images in Figure 3, a d-spacing of 0.34 nm was observed within both V$_2$O$_5$ EO-300 CB and V$_2$O$_5$ EO-300 GH, which is corresponding to the (110) lattice plane in orthorhombic V$_2$O$_5$.[21] But the morphologies of V$_2$O$_5$ nanoparticles in V$_2$O$_5$ EO-300 CB and V$_2$O$_5$ EO-300 GH are quite different, e.g. spherical in V$_2$O$_5$ EO-300 CB and platelet-like in V$_2$O$_5$ EO-300 GH. It is likely that the morphology of the additives (spherical CB and platelet-like GH) can affect the shapes of V$_2$O$_5$ nanoparticles using such a sol-gel chemistry method. Electron diffraction analysis confirms that V$_2$O$_5$ nanoparticles in V$_2$O$_5$ EO-300 CB and V$_2$O$_5$ EO-300 GH membranes are of crystalline orthorhombic phase (S3).

Raman spectra of V$_2$O$_5$ EO-400 CB, EO-300 CB and EO-300 GH are fully consistent with pure orthorhombic V$_2$O$_5$ reference (Figure 4a).[22] G and D Raman peaks from graphitic materials can’t be seen because the content of carbon is low and the background scattering is very strong due to the highly porous structure. Powder X-ray diffraction data further confirm the formation of
crystalline orthorhombic V$_2$O$_5$ (JCPDS 41-1426) in all types of asymmetric membranes annealed in air (Figure 4b). The peaks of V$_2$O$_5$ asymmetric membranes are much broader than those of micron-size V$_2$O$_5$ reference, indicating the presence of nanoscale V$_2$O$_5$ particles. The sharp peak at 27° from V$_2$O$_5$ EO-300 GH sample is ascribed to graphitic materials.[23] It is notable that V$_2$O$_5$ EO-300 CB sample also has a peak centered around ~27°, which may be due to the presence of trace amount of V$_4$O$_7$ or graphitic materials.[8] This peak didn’t show up for V$_2$O$_5$ EO-400 CB where carbon content is much lower.

The XPS spectra of V 2p are shown in Figure 5. The peaks centered at 517.2 and 524.7 eV are ascribed to V$^{5+}$ 2p$_{3/2}$ and V$^{5+}$ 2p$_{1/2}$, respectively.[24] The weak shoulder peaks around 516 eV may be generated by trace amount of V$^{4+}$ that were produced during the carbonization process and not able to be fully oxidized into V$^{5+}$ during the following annealing in air.[25] It is also possible that V$^{5+}$ can be slowly reduced into V$^{4+}$ by the X-ray beam during XPS measurements as reported by Pinna et al.[26] Noteworthy, V$^{4+}$ was not able to be detected by HRTEM, PXRD and Raman in our study, due probably to its low concentration.

The content of active materials vanadium pentoxide in these carbonized asymmetric membranes was determined using thermogravimetric (TGA) analysis (Figure 6). The mass percentages of V$_2$O$_5$ were calculated to be 94.54, 91.44 and 74.7 wt. % in V$_2$O$_5$ EO-400 CB, V$_2$O$_5$ EO-300 CB and V$_2$O$_5$ EO-300 GH, respectively. The lower content of carbon in V$_2$O$_5$ EO-400 CB is due to the rapid oxidation of carbon at 400°C than 300°C in air. The content of carbon in
V$_2$O$_5$ EO-300 GH is much higher than other two types of membranes because it requires higher temperature to oxidize crystalline graphene.[27] Calculated by Brunauer–Emmett–Teller (BET) method (Table 1), the specific surface areas of V$_2$O$_5$ EO-400 CB, V$_2$O$_5$ EO-300 CB and V$_2$O$_5$ EO-300 GH were found to be 42.5, 21.7 and 20.5 m$^2$ g$^{-1}$, respectively. The higher specific area of V$_2$O$_5$ EO-400 CB is possibly caused by the more carbon loss during annealing which can create more nanopores. Barrett-Joyner-Halenda (BJH) pore size distribution data indicate that there are both nanopores and macropores ranging from several nanometers to more than one micron (S4). Since the nanoporous skin layer provides the salt rejection function, this type of membrane is defined as nanoporous (or nanofiltration) membrane by the membrane society even though there are macropores. Herein we abide by this conventional rules regulated by the membrane society.
3.3. Electrochemical properties of V$_2$O$_5$ asymmetric membranes as LIB cathodes

Electrochemical performance of V$_2$O$_5$ cathodes is shown in Figure 7. All three membrane cathodes demonstrate excellent rate performance, which can be attributed to the high surface area, nanoporous structure and conductive carbon coating on V$_2$O$_5$ nanoparticles. These cathodes delivered a capacity close or above 200 mA h g$^{-1}$ at 20 mA g$^{-1}$, which is much higher than conventional ones.[1] Although the initial capacity of V$_2$O$_5$ EO-400 CB cathode is highest (174 mA h g$^{-1}$ at 100 mA g$^{-1}$) as shown in Figure 7b mainly due to its high surface area,[28] the capacity fades more rapidly as compared to other two membranes, i.e., 7 % decrease after 120 cycles at 100 mA g$^{-1}$ (Figure 7b). However, such cyclability is still excellent in comparison with traditional

### Table 1. BET surface areas of three types of V$_2$O$_5$ asymmetric membranes.

<table>
<thead>
<tr>
<th>Type of membrane</th>
<th>BET specific Area (m$^2$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V$_2$O$_5$ EO-400 CB</td>
<td>42.5</td>
</tr>
<tr>
<td>Heated up to 400 °C in air in 5 mins</td>
<td></td>
</tr>
<tr>
<td>V$_2$O$_5$ EO-300 CB</td>
<td>21.7</td>
</tr>
<tr>
<td>Heated at 300 °C in air for 1.5 hrs</td>
<td></td>
</tr>
<tr>
<td>V$_2$O$_5$ EO-300 GH</td>
<td>20.5</td>
</tr>
<tr>
<td>Heated at 300 °C in air for 1.5 hrs</td>
<td></td>
</tr>
</tbody>
</table>
cathode materials. In comparison, V\textsubscript{2}O\textsubscript{5} EO-300 CB cathode demonstrates an initial capacity of 159 mAh g\textsuperscript{-1} at 100 mA g\textsuperscript{-1}, which increases slightly by \textasciitilde8\% in the first 150 cycles and then degrades gradually to 133 mAh g\textsuperscript{-1} after 380 cycles (84\% capacity retention as compared to the first cycle). V\textsubscript{2}O\textsubscript{5} EO-300 GH cathode demonstrates the most outstanding cycling performance. The capacity actually gradually increases by \textasciitilde8\% throughout 380 cycles, indicating that V\textsubscript{2}O\textsubscript{5} can be more efficiently lithiated during the cycling process. It is believed that the flexible graphene networks surrounding V\textsubscript{2}O\textsubscript{5} NPs benefit an enhanced conductivity and structural stability, thus allowing for repeated volume expansion and efficient lithium insertion and extraction.[3] This protection is further improved by the porous asymmetric membrane structure, resulting in excellent capacity retention and rate performance.

The control asymmetric membrane (V\textsubscript{2}O\textsubscript{5} EO-300 without CB or GH) also demonstrates an excellent cycling stability (S5). This fact further supports that the porous asymmetric membrane structure can efficiently stabilize the lithiation and delithiation process in V\textsubscript{2}O\textsubscript{5}-based cathode (S5). However, the overall capacity is very low (<60 mAh g\textsuperscript{-1} at 100 mA g\textsuperscript{-1}, S5) because the V\textsubscript{2}O\textsubscript{5} particles have relatively large sizes (~200 nm, S5) and there is a lack of conductive additives. Recall that V\textsubscript{2}O\textsubscript{5} has extremely low lithium diffusivity and poor electron conductivity as compared to other conventional cathode materials. It is believed that the nanoscale conductive additives such as GH or CB powders can function as extra nucleation sites to generate smaller particles and also increase the electrode conductivity. In other words, the lack of these conductive particles can lead to the formation of larger V\textsubscript{2}O\textsubscript{5} powders in V\textsubscript{2}O\textsubscript{5}
asymmetric membrane without using CB or GH additives and the generation of low conductivity electrode.

The initial capacity increase in the $V_2O_5$ EO-300 CB and $V_2O_5$ EO-300 GH may be ascribed to volume expansion in the electrodes which opened up some closed pore and enabled more $V_2O_3$ accessible for lithiation and delithiation. The continuous capacity increase and outstanding stability in $V_2O_5$ EO-300 GH implies the existence of grapheme renders excellent structural and mechanical stability over CB where capacity started decreasing after 150 cycles in $V_2O_5$ EO-300 CB cathodes. Figure 7c and 7d show that the normalized voltage profiles. The gap between the charge and discharge plateaus represents the polarization. The polarization in the $V_2O_5$ EO-300 GH cathodes is lower than $V_2O_5$ EO-300 CB cathode in the first cycle. For example, the polarization at 0.5 normalized capacity is 0.36 V and 0.29 V for $V_2O_5$ EO-300 CB and $V_2O_5$ EO-300 GH, respectively. The polarization further reduces to 0.24 V after 380 cycles for $V_2O_5$ EO-300 GH at 0.5 normalized capacity. In contrast, the polarity increases slightly up to 0.48 V for $V_2O_5$ EO-300 CB after 380 cycles. The polarization changes in $V_2O_5$ EO-300 GH and $V_2O_5$ EO-300 CB cathodes explain the difference in their cyclability behaviors in Figure 7b.

The cyclic voltammetry (CV) of $V_2O_5$ EO-300 CB and $V_2O_5$ EO-300 GH membrane electrodes are shown in Figure 8. For $V_2O_5$ EO-300 CB electrode, three lithiation peaks centered at 3.36, 3.16 and 2.23 V are ascribed to the phase transitions of
(α ↔ ε), (ε ↔ δ) and (δ ↔ γ), respectively.[4] The corresponding electrochemical reactions are as follows (Eq. (1-3)):

\[
\begin{align*}
V_2O_5 + 0.5Li^+ + 0.5e^- & \leftrightarrow Li_{0.5}V_2O_5 \quad (\alpha \leftrightarrow \varepsilon) \quad (1) \\
Li_{0.5}V_2O_5 + 0.5Li^+ + 0.5e^- & \leftrightarrow LiV_2O_5 \quad (\varepsilon \leftrightarrow \delta) \quad (2) \\
LiV_2O_5 + Li^+ + e^- & \leftrightarrow Li_2V_2O_5 \quad (\delta \leftrightarrow \gamma) \quad (3)
\end{align*}
\]

The 2.23 V lithiation peak is positively shifted during CV cycling especially for V2O5 EO-300 CB, indicating an increasing conductivity which is consistent with the reduced impedance as shown in Figure 9a. This fact is also consistent with the voltage profiles shown in Figure 7c and d, where the polarization reduces after cycles. Three delithiation peaks around 2.60, 3.26 and 3.46 V are assigned to (γ ↔ δ), (δ ↔ ε) and (ε ↔ α) phase transitions, respectively. Additionally, the large voltage difference between lithiation and dethiation reactions corresponding to Eq. (3) implies that it is quite resistive for lithium ions to diffuse out of Li2V2O5. The broad anodic peaks around 2.4 and 2.7 V and cathodic peaks around 2.4 and 2.8 V have previously been observed from V2O5 nanomaterials that were synthesized using sol-gel methods.[29-31] These peaks suggest that there is a concentration gradient of Li+ in V2O5 crystals.[32,33] Since the resistance of lithium insertion and extraction varies for V2O5 particles of different sizes, it can result in over potential difference and thus generate multiple broad peaks. The resistance variation becomes more serious during the δ/γ phase transition because lithium diffusion coefficient (D_{Li}) decreases from around 3.3 × 10^{-9} \text{ cm}^2 \text{s}^{-1} for low lithium content (ε/δ) to 1×10^{-10} \text{ cm}^2 \text{s}^{-1} at high lithium
content ($\gamma/\delta$).[4] By strictly controlling the size and size distribution, the multiple broad peaks related to the $\gamma/\delta$ phase transition with variable intercalation resistances could be converted into a single sharp peak.

EIS spectra of V$_2$O$_5$ EO-300 CB and V$_2$O$_5$ EO-300 GH cathodes are shown in Figure 9. It can be clearly seen that the charge transfer resistance was significantly changed for V$_2$O$_5$ EO-300 CB after the cycling test, implying that there was a dramatic electrode evolution during the cycling. In addition, the ohmic resistance increased after cycles for V$_2$O$_5$ EO-300 CB, probably due to the partial electrode detachment from the current collector after repeated cycles. In comparison, the EIS spectra of V$_2$O$_5$ EO-300 GH are very similar to each other before and after the cycling test. This fact supports that the electrode is integral and SEI layer is highly stable during the repeated lithiation/delithiation. It should be pointed out that the dissolution of vanadium has been previously observed especially at higher discharge rates, which can lead to rapid capacity loss and increased cell resistance.[4,34,35] The dissolution can be significantly relieved by using moderate discharge rates and adopting advantageous morphology.[3,9,10,15] The improved cyclability from V$_2$O$_5$ EO-300 GH suggests that the V leaching could be more reduced as compared to V$_2$O$_5$ EO-300CB electrode.

4. Conclusions

Three types of V$_2$O$_5$ asymmetric membranes are fabricated using an adapted phase inversion method combined with sol-gel chemistry. The three-dimensional nanoporous
structure and carbon coating can dramatically improve the electrochemical performance of V$_2$O$_5$-based cathodes. The annealing temperature and choice of conductive additives also have a significant impact on the cycling performance. High-temperature annealing can shorten the cycling life due to the large loss of conductive additive at elevated temperatures. The addition of GH benefits electrode stability and also affects the morphology of V$_2$O$_5$ nanoparticles. The nearly 100% capacity retention after 380 cycles, straightforward fabrication process and excellent rate performance make this method outstanding from other approaches in literature.

5. Acknowledgements

Financial and infrastructural supports from Georgia Southern University are sincerely acknowledged by JW, IB, HC and TC. TC deeply appreciates the 206-2017 GSU COUR award. We thank Dr. Cliff Padgett for his kind helps with the PXRD measurements at Armstrong State University and Dr. Quirino for the use of Raman spectroscopy at GSU. C.J. thanks the support provided by Analytical and Diagnostics Laboratory Small Grant Award from State University of New York at Binghamton and the useful discussion with Prof. Guangwen Zhou. RB thanks the funding provided by NSF-CHE 1359229 (REU) at Georgia Southern University. RB is a REU research student at GSU, who originally comes from Spring Hill College, LA. The TEM work shown in S3 was conducted in the William R. Wiley Environmental Molecular Sciences Laboratory (EMSL), a national scientific user facility sponsored by DOE’s Office of Biological and Environmental Research and located at PNNL. PNNL is
operated by Battelle for the Department of Energy under Contract DE-AC05-76RLO1830.

References:

Figure 1. a) Schematic of V₂O₅ asymmetric membrane fabrication; b) photo image of V₂O₅ asymmetric membrane (top view); and c) scanning electron microscope (SEM) image of V₂O₅ asymmetric membrane (cross-sectional view).
Figure 2. SEM images of V$_2$O$_5$ EO-400 CB membrane a) top-view and b) cross-sectional view; V$_2$O$_5$ EO-300 CB membrane c) top-view and d) cross-sectional view; and V$_2$O$_5$ GH EO-300 GH membrane e) top-view and f) cross-sectional view. Scale bars are 1 µm for a, c, e and 10 µm for b, d, f.
Figure 3. High resolution transmission electron microscope images of a) V$_2$O$_5$ EO-300 CB and b) V$_2$O$_5$ EO-300 GH membranes. Scale bars are 5 nm.
Figure 4. a) Raman spectra and b) powder X-ray diffraction patterns of various V$_2$O$_5$ asymmetric membranes.
Figure 5. X-ray photoelectron spectroscopy spectra of various V$_2$O$_5$ asymmetric membranes. Note: pure V$_2$O$_5$ particles are used as a reference.
Figure 6. Thermogravimetric analysis of various V$_2$O$_5$ asymmetric membranes using compressed air as the purging gas a) V$_2$O$_5$ reference, b) V$_2$O$_5$ EO-400 CB, c) V$_2$O$_5$ EO-300 CB and d) V$_2$O$_5$ EO-300 GH.
a

![Graph a](image1)

- **Capacity (mAh g⁻¹)**
- **Cycle Number**
- **V₂O₅ EO-400 CB**
- **V₂O₅ EO-300 CB**
- **V₂O₅ EO-300 GH**

b

![Graph b](image2)

- **Capacity (mAh g⁻¹)**
- **Cycle Number**
- **V₂O₅ EO-400 CB**
- **V₂O₅ EO-300 CB**
- **V₂O₅ EO-300 GH**
- **100 mA g⁻¹**
Figure 7. Electrochemistry data of three types of membrane electrodes a) C-rate performance, b) long term performance at a current density of 100 mA g\(^{-1}\), c) and d) voltage profiles of V\(_2\)O\(_5\) EO-300 CB and V\(_2\)O\(_5\) EO-300 GH membranes at 100 mA g\(^{-1}\) at 1\(^{st}\) and 380\(^{th}\) cycles, whose capacities are normalized to their corresponding maximum capacities for convenient polarization comparison. The standard deviation bars in a) were obtained from three pieces of membranes of each type.
Figure 8. Cyclic voltammetry of a) V$_2$O$_5$ EO-300 CB and b) V$_2$O$_5$ EO-300 GH membrane electrodes (5 cycles).
Figure 9. Nyquist plots of EIS for a) V$_2$O$_5$ EO-300 CB and b) V$_2$O$_5$ EO-300 GH membrane electrodes.