

Flexible and free-standing electrode for high-performance vanadium redox flow battery: Bamboo-like carbon fiber skeleton from textile fabric

Rajesh Madhu^{a,b,*}, Fedor V Kusmartsev^a, Kue-ho Kim^b, Hyo-Jin Ahn^{b,*}

^a Department of Physics, Khalifa University, 127788 Abu Dhabi, UAE

^b Department of Materials Science and Engineering, Seoul National University of Science and Technology, Seoul 01811, South Korea

ARTICLE INFO

Keywords:

Redox-flow battery
COTTON textiles
Carbon cloth
Flexible electrodes
Redox potential
Energy efficiency

ABSTRACT

Developing the free-standing and flexible electrodes with high current density and cycle stability is still under debate towards the extensive application of vanadium redox flow batteries (VRFBs). So far, carbon felts, carbon fibers and carbon papers are used which mostly prepared from fossil precursors make them unsustainable. Herein, we first sought to prepare a mechanically flexible and free-standing carbon cloth from terry cloth towel fabric (100% cotton) by using a simple pyrolysis method (TCC). Interestingly, we obtained a bamboo-like carbon fiber structure with a well-balanced micro-, meso-, and macro porosity. Moreover, a low-cost Polyethyleneimine (PEI) is used for Nitrogen doping on carbon cloth skeleton (N-TCC) to improve its electrochemical performance. The as-prepared N-TCC were utilized as efficient electrodes for the VRFBs with higher electrochemical activity towards vanadium species $\text{VO}_2^+/\text{VO}^{2+}$ than TCC and commercial graphite felt (GF) in a 3 electrode electrochemical cell *i.e.* half-cell. Interestingly, the VRFBs constructed with N-TCCs electrodes (both +ve and -ve half cells) in a full cell configuration at varied current densities from 40 to 160 mA cm^{-2} , we achieved an increased energy efficiency (EE), voltage efficiency (VE), and columbic efficiency (CE) compared to pristine CFs, and TCC based VRFBs. The newly designed cotton based electrodes establishes a unique opportunity for constructing a low-cost, metal-free VRFBs towards a large-scale commercialization of sustainable energy storage system.

1. Introduction

Redox flow batteries (RFBs), one of the most promising large-scale energy storage devices [1–5] which possesses high energy efficiency, rapid response, scalability, long cycle life, safety, eco-friendly, and they allow for independent scaling of power and storage capacity surpassing the conventional batteries and commercially successful in industries [6–10]. The capacity is related to the volume and concentration of the electrolyte while the power is related to the electrode size and stack cell numbers. Moreover, the RFBs do not employ the intercalation reactions of Li-ion batteries resulting no morphological change of the electrode during charge/discharge without same capacity fade mechanisms leads to achieve longer lifetimes. The major issue of the RFBs is the cross-over contamination among the anode and cathode electrolytic compartments. In contrast, vanadium redox flow battery (VRFB) has been the most successful in commercialization, limiting the severe cross-over contamination [11] attributed to the same vanadium element with different oxidation states is adopted in both positive and negative electrolyte tanks. However, VRFBs still needs to be developed by

improving their energy efficiencies and lifetimes leads to reduce their cost [12]. Electrode plays an important role in VRFBs, which determining the kinetic parameters performance of the system, because the power of the system related to the rate of reaction of the redox species at the electrodes which provides the reaction sites for those redox couples and also affects the ion-mass transport inside the porous structure. In VRFBs, graphite felts (GFs) and carbon papers (CPs) are widely used as the free-standing electrode material due to their higher electronic conductivity, long-term stability, corrosion resistance, and large porosity with wide potential window. However, these GF and CP materials have been mostly derived from fossil precursor such as polyacrylonitrile (PAN) with high temperatures that hinders overall sustainability. Moreover, those GFs electrodes are relatively high cost and shows poor kinetics on vanadium redox reactions and poor wettability, resulting in poor rate performance in the VRFB system. Hence, it is highly imperative to improve the common utilized carbon-based electrodes to enhance their electrocatalytic activity, allows to hugely improve the cell performance without undesirable side reactions like hydrogen evolution reaction and consequently reduce the costs of the battery system in

* Corresponding authors.

E-mail addresses: rajesphysics@gmail.com, r.madhu@imperial.ac.uk (R. Madhu), hjahn@seoultech.ac.kr (H.-J. Ahn).

<https://doi.org/10.1016/j.electacta.2022.141619>

Received 29 August 2022; Received in revised form 17 October 2022; Accepted 26 November 2022

Available online 30 November 2022

0013-4686/© 2022 Elsevier Ltd. All rights reserved.

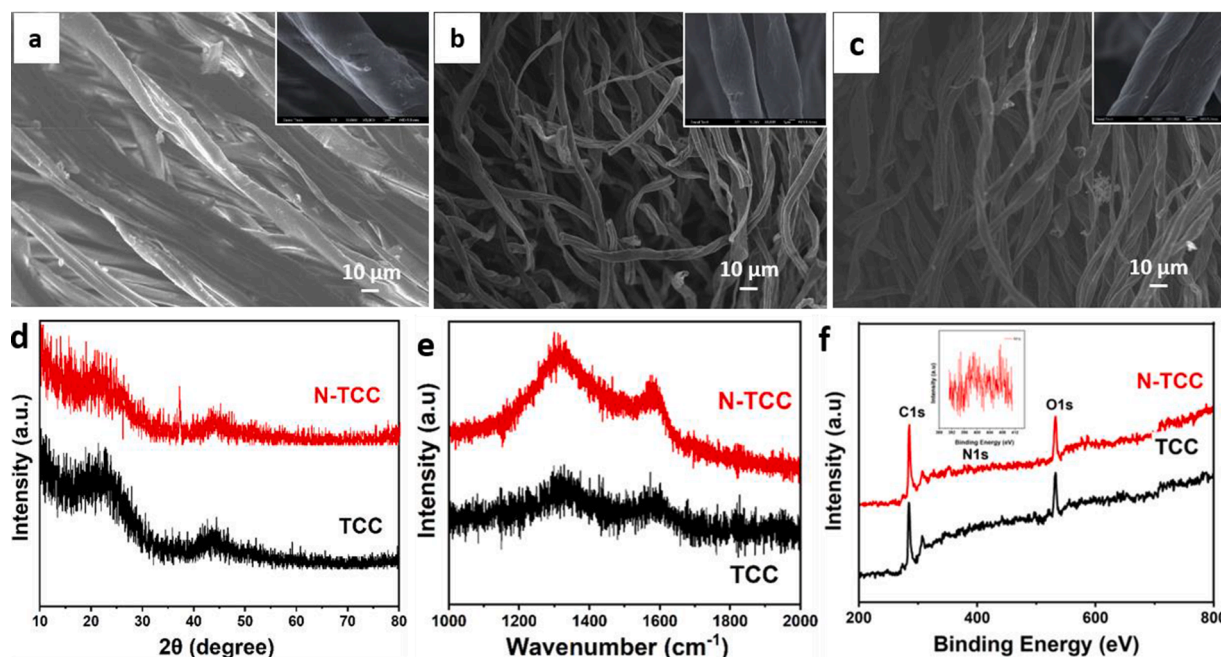


Figure 1. a-c) SEM images of cellulose fibers of Terry Cloth Towel, carbon fibers of TCC, and N-TCC respectively. e,f) XRD, XPS survey spectra of TCC, N-TCC (inset-N1s).

terms of reducing stack cell size. Sustainable precursors are of high interest in producing large-scale and low-cost carbon based electrodes with numerous chemical functionalities for energy devices applications [13–15]. Natural cotton microfiber fabrics consisting mainly of plant cellulose fibers widely utilized for producing soft and breathable textile and clothing [16]. An evolving research on cotton fabrics with tremendous functionalities intrigued to fabricate the free-standing carbon electrodes as wearable platform for several applications [16–19]. These cotton fabric derived carbon cloth possesses unique properties such as high surface area, high electrical conductivity, excellent mechanical and chemical durability widely utilized as wearable electrodes for supercapacitor energy devices [18–24]. However, to the best of our knowledge, there is no electrochemical investigations are reported towards natural cotton fabric electrode for this VRFB application.

Herein, we first report the direct conversion of conductive and flexible carbon cloth electrode from terry cloth towel fabric (100% natural cotton) by using a simple pyrolysis method (TCC) and tested for all-vanadium redox flow battery. Notably, we used Polyethyleneimine (PEI) for the nitrogen doping on carbon cloth skeleton (N-TCC) to further enhance its electrocatalytic activity.

2. Experimental

2.1. Materials

Terry cloth towel (100% natural cotton) purchased from a local convenient store. The heat-treated graphite felt (HT-GF) with 4.7 mm of thickness was purchased from MIRPA Corp. Nafion 212 membrane was purchased from NARA Cell-Tech Corp, South Korea. Polyethyleneimine (50 wt% in H₂O), and sulfuric acid (95–98%) were obtained from Sigma Aldrich. Vanadium (IV) sulfate oxide hydrate (99.9%) was purchased from Alfa Aesar.

2.2. Synthesis of the TCC and N-TCC electrodes

High surface area Towel-derived Carbon Cloth (TCC) was prepared by a simple soaking, drying, and pyrolysis process (Fig. S1a). Sodium halides are widely used as a soft salt template and activating agent to

prepare hierarchical porous carbons. In this work, we used sodium fluoride (NaF) as a surface activating agent to introduce some roughness/defects and/or pores during carbonization step [20]. We have included additional notes as required in the manuscript. Firstly, a large piece of waste terry cloth towel (100% cotton; 20 × 20 cms size) was immersed into 1 M NaF solution as an activating agent and to remove any moistures for 1h and dried in an air oven at 100°C for 6h. The as-dried cloth carbonized at 800°C in a horizontal tubular furnace for 1h under N₂ gas flow with a heating rate of 3°C min⁻¹. The as-activated carbon fabric washed by soaking the free-standing and highly flexible carbon cloth in DI water bath under heating (80°C) and stirring for 1 h followed by rinsing with ethanol and DIW several times to remove Na nanocrystals together with any impurities in the fiber surface which can create small nanopores (Named as TCC). Further, 2 mL of PEI (50 wt% in H₂O) was mixed in 50 mL of water under vigorous stirring. And a piece of TCC was immersed in the above-mentioned PEI solution and heated at 60°C for 6h in the fuming hood. After cooling down, the wet carbon cloth was rinsed with water and dried (100°C) and further annealed at 800°C in a horizontal tubular furnace for 2h under N₂ gas flow with a heating rate of 3°C min⁻¹ and finally washed with HCL (to remove any moisture) and deionized water (DIW) and dried overnight (Named as N-TCC).

2.3. Electrochemical measurements

Cyclic voltammetry (CV) measurements were performed with an AUTOLAB, USA workstation, which the voltage window of -1.0 V to 1.6 V at scan rate of 5 mV s⁻¹ in a three-electrode cell configuration. The electrolyte for CV test was prepared (optimized condition) by diluting 1.5 mL of 1.5 M V₂SO₄ in 3 M H₂SO₄ into 28.5 mL of DIW. N-TCC as working electrodes, a saturated calomel electrode as the reference electrode, and a Pt mesh used as a counter electrode. A glassy carbon electrode holder used to connect the punched carbon cloth (0.6 cm²).

To measure galvanostatic charge-discharge (GCD) performance, we used the VRFB cell (MIRPA corp., USA) which consists PVC cover plates, Au coated Cu current collectors, two graphite bipolar plates and two PTFE frames (5 mm thickness) with 2 × 3 cm cell central opening were employed in the single cell configuration. The thin TCC and N-TCC

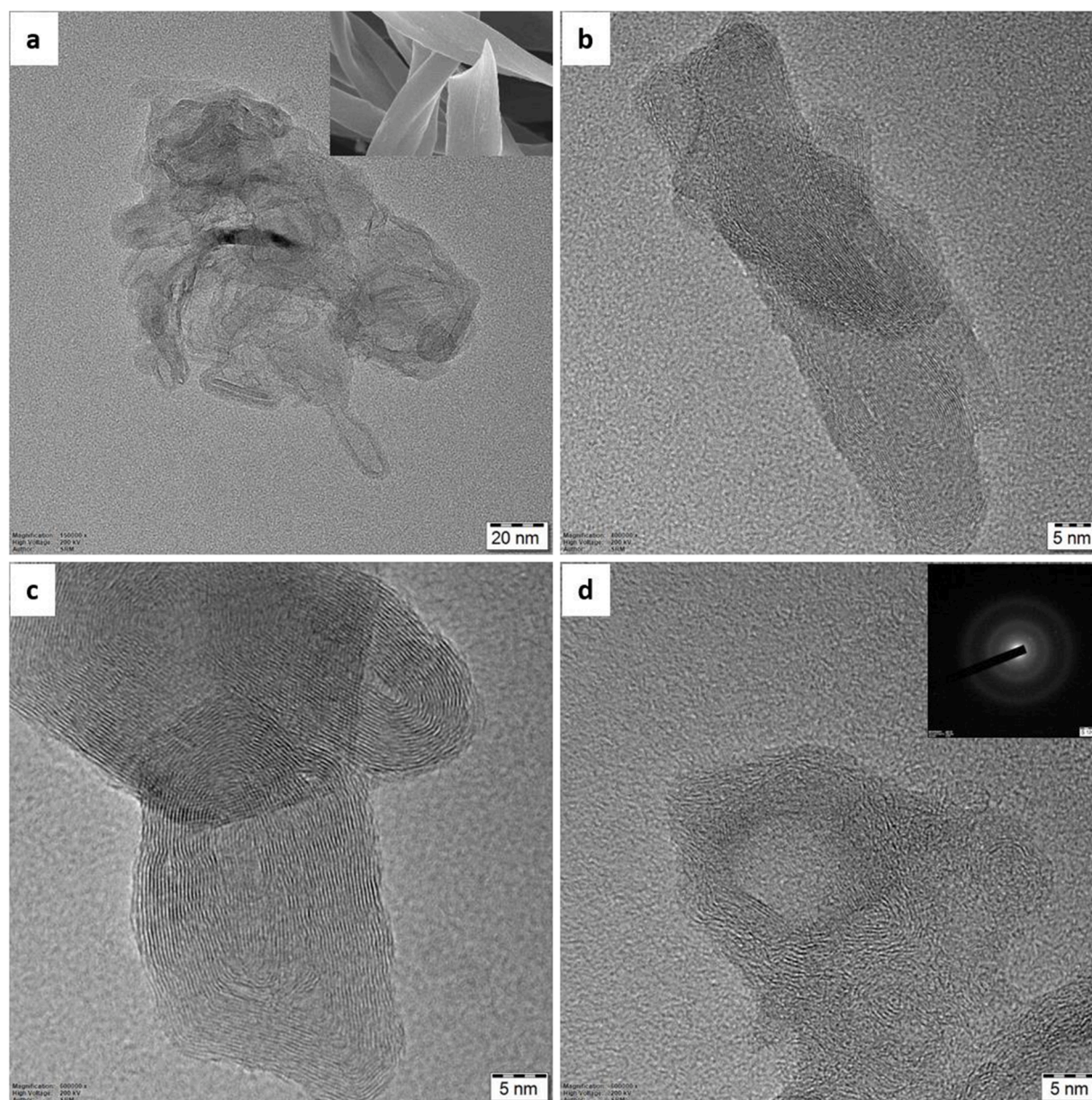


Figure 2. a-c) TEM images of NTCC sample with bamboo-like carbon structures at different magnifications. d) SAED pattern of NTCC sample.

electrodes were placed on top of the thick HT-GF and separated by a Nafion-212 cation exchange membrane. The Nafion-212 membrane was soaked in DIW for 24 h prior to the VRFB single cell test. For comparison, we also performed the VRFB with only HT-GF. Fig. S1b shows the photographs of the VRFB system used in the present study. 20 mL of 1.5 M V_2SO_4 in 3 M H_2SO_4 electrolyte was used on negative side while 22 mL used in positive side to avoid overcharging the positive electrolyte. The electrolytes were recirculated from the containers (100 mL) by using a two-channel peristaltic pump with the flow rate of 30 ml min^{-1} on both sides. Firstly, the battery was pre-charged up to 1.7 V at 40 mA cm^{-2} . Then the positive electrolyte was removed and refilled by fresh electrolyte and cycled at various current densities from 40 to 160 mA cm^{-2} with the cut-off voltage from 1.7 V (for charging) to 0.5 V (for discharging). All the single cell experiments were performed with under N_2 purge state condition.

3. Results and discussion

3.1. Materials characterizations

Fig. S1a shows the fabrication of N-TCC from Terry cloth towel by a simple soaking, drying, folding and carbonization process. Fig. S1b shows the photographs of full cell set up and their components and electrodes with N-TCC and Nafion 212 membrane.

A large piece of cotton cloth is soaked with NaF and dried in an oven for overnight and folded the dried cotton cloth for the carbonisation at high temperature and soaked and washed with HCL and DIW to obtain the carbon cloth for the further characterisations. The morphological characterization of commercial cotton towel, TCC and N-TCC performed by scanning electron microscopy (SEM) as shown in Fig. 1a-c, which reveals that the commercial cotton towel textile consists of interwoven cellulose fibers (5–10 μm). Fig. 1b and 1c shows the SEM images of TCC and N-TCC interlayers, retains the knitted structure with shrinking diameters of the carbon fibers are comparable to those of cellulose fibers in the Terry cloth towel textile (Fig. 1a). Moreover, there is no visible

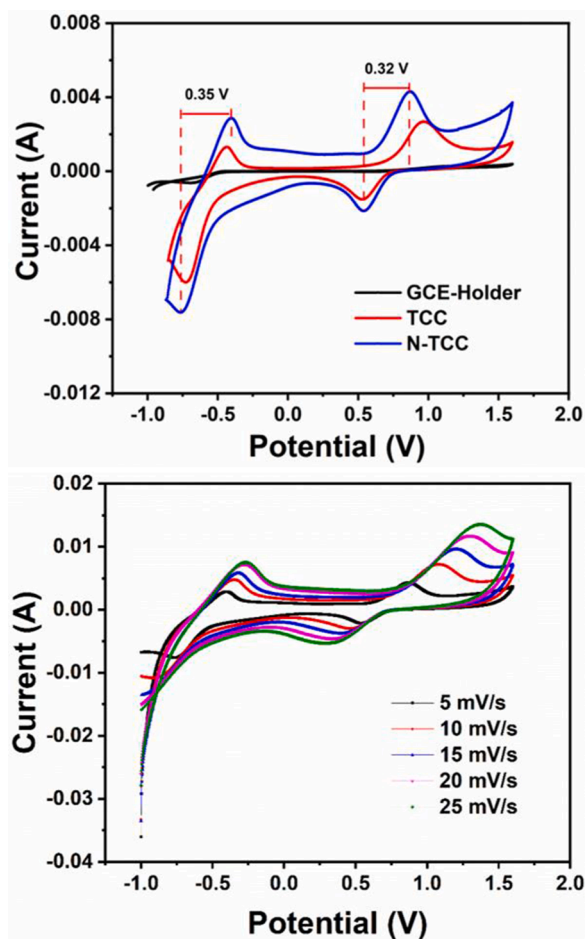


Figure 3. a) CVs of different electrodes in V electrolyte. Voltage window of -1.0 V to 1.6 V at scan rate of 5 mV s⁻¹ in a three-electrode cell configuration. The electrolyte for CV test was prepared 0.15 M V₂SO₄ in 0.3 M H₂SO₄ (under optimum concentration). B) CV profiles of N-TCC electrode recorded at different scan rates.

morphological changes on the surface of the nitrogen doped carbon cloth (N-TCC) when compared to TCC. As can be seen, the surface of the carbon cloth was not physically changed or damaged after the surface treatment of the proposed nitrogen doping by a simple stirring and heating, and thermal decomposition with PEI content which reveals that our TCC cloth is highly suitable for N-doping and further confirmed with XRD study. Fig. 1d shows the XRD study of the TCC and N-TCC, resulted with two prominent peaks for both samples at 23.6° and 43.7° corresponding to the (002) and (100) planes, respectively. The XRD results suggests the disordered graphene in the internal carbon fiber structure and there is no noticeable difference on crystal structures of N-TCC when compared with TCC. However, the corresponding peaks of N-TCC has slightly broader and the peak intensity become weaker suggesting that the carbon fiber structure become a bit more disordered after N doping. This indicates that N content has a great influence on the carbon fiber structure which is more favourable for the electrochemical redox reaction kinetics [25].

Fig. 1e shows the XPS survey spectra of the N-TCC sample which confirmed the presence of surface C, O, and N species. The results further reveals that TCC and N-TCC samples mainly composed of 80 at% of C, high O content (18 at%), and 2 at% of N will be highly favourable for electrochemical redox reactions. As shown in Fig. S2a, there are 3 deconvoluted C1 peaks of N-TCC sample was obtained at 283 eV, 284.8, 287.6 corresponding to C–N (ref), C–C, and O–C–O bond. There are 3 types of oxygen atoms existed in carbons, such as (i) C=O quinone-type

oxygen (O–1, 531 eV); (ii) C–OH phenol groups and/or C–O–C ether groups (O–2, 532 eV); and (iii) COOH chemisorbed oxygen and/or water (O–3, 533 eV). Among the three types of oxygen atoms in the carbons, specifically the quinone oxygen is electrochemically active in acidic electrolytes. Interestingly, as shown in Fig. S2b, the O 1s core level spectrum of N-TCC clearly reveals the presence of COOH (529.5 eV), C=O quinone type oxygen species (530.6 eV) and C–O–C (532.5 eV) [26]. The as-prepared N-TCC electrodes are mechanically flexible, and more stable with several folding condition which is highly desirable free-standing electrodes in VRFB system.

Fig. 1f shows the RAMAN spectrum of TCC and NTCC samples which represents the two distinct peaks at ~ 1330–1335 cm⁻¹ (D-band) and 1585 cm⁻¹ (G-band). Moreover, the intensity of D band is higher than the G band which suggesting the disordered and amorphous structure, while G band represents the tangential mode of the sp² carbon hexagonal lattice. The intensity ratio (I_D/I_G) of the NTCC is slightly higher than TCC suggesting the presence of large defects with more amount of oxygen moieties with massive defects, i.e. existing edges and holes which is highly consistent with XPS and further confirmed by TEM.

As shown in Fig. 2a–d, the TEM images of NTCC clearly reveals the elongated conical shaped bamboo-like structure with a turbostratic graphite structure with an average lattice fringe interlayer d-spacing of 0.1 nm. The SAED pattern (inset; Fig. 2d) is more consistent with the XRD result which shows the corresponding to 002 and 100 planes. Hence, the functionalization (N-doping) of carbon structure leads to increase the number of active redox sites due to their easy wettability with improved electrode kinetics resulting in achieving the higher VRFB performance with enhanced energy efficiencies and lowering the activation overpotentials.

3.2. Cyclic voltammetry (CV) measurements

To test the effect of nitrogen-functional groups of the carbon cloth electrodes towards the VO²⁺/VO₂⁺ and V²⁺/V³⁺ redox reactions, CV tests were performed and corresponding electrochemical parameters are listed in Table S1. Fig. 3a shows the CVs of TCC, N-TCC and bare GCE holder recorded between the potential range of -1.0 to 1.6 V. Notably, we obtained well-defined redox peaks corresponding to two redox couples with several fold increased current densities for N-TCC electrode over TCC and bare GCE holder. As shown in CV profiles, for the positive electrode, the oxidation peak corresponding to VO²⁺ and VO₂⁺ is obtained at 0.86 V, and the reduction peak observed at 0.54 V. Interestingly, we obtained a very low oxidation peak potential for N-TCC electrode than TCC and bare GCE holder, and notably we achieved a very low potential difference (anodic and cathodic peak) which highly comparable to several reports on carbon based VRFB [15, 27–30]. For the negative electrode, the oxidation peaks associated with the V²⁺ to V³⁺ is obtained at 0.4 V and the corresponding reduction peak obtained at 0.75 V. The obtained electrochemical reaction kinetics over N-TCC electrode reveals that the presence of nitrogen and various oxygen functional groups on the carbon fiber network can greatly accelerate the redox reaction resulted with a well-defined redox peaks for both VO²⁺/VO₂⁺ and V²⁺/V³⁺ redox reactions. Fig. 3b shows the CV profiles at different scan rates ranging from 5 to 25 mVs⁻¹. It is well noted that the corresponding oxidation peaks potentials are shifted to higher potentials and reduction peaks potentials are shifted to lower potentials. The expected potential differences of each redox couple is a good indication of the redox reactions kinetics and excellent reversibility with high polarization associated to the conductivity of the N-TCC electrode.

The as-prepared flexible TCC and N-TCC electrodes were evaluated in VRFBs and each cell has been charged and discharged under varied current density (40 to 160 mA cm⁻²). As shown in Fig. 4a, it is noted that the VRFB cell with both positive and negative N-TCC electrodes exhibited with a lower IR drop for a cycle even at high current density when compared to TCC and bare GF which indicates the favourable reduced electrochemical polarization with nitrogen incorporation on

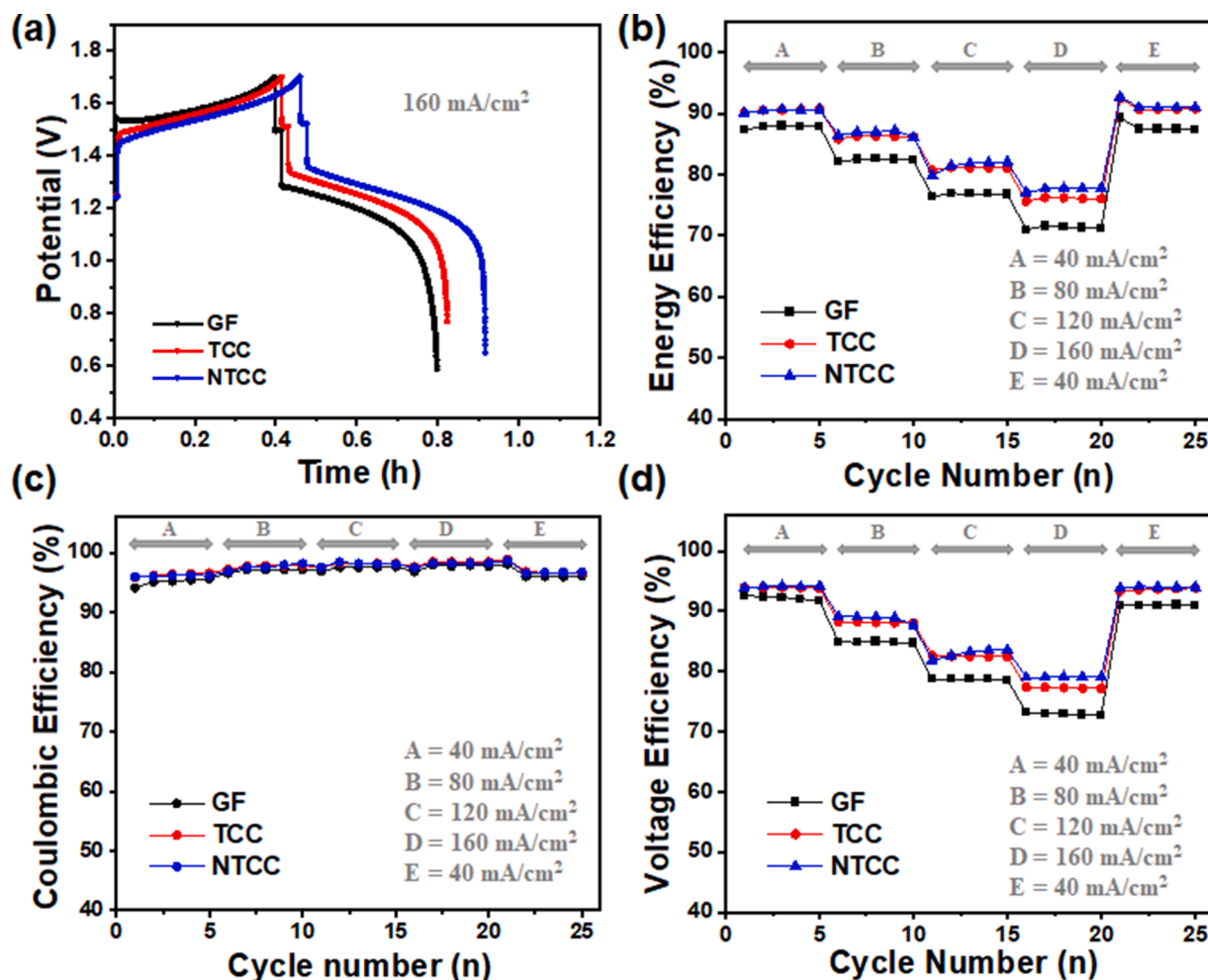


Figure 4. a) GCD profiles of GF, TCC, and N-TCC electrodes. b) energy efficiencies, c) coulombic efficiencies, d) voltage efficiencies of GF, TCC and N-TCC measured at various current densities of 40 mA cm^{-2} (A=1–5 cycles), 80 mA cm^{-2} (B=6–10 cycles), 120 mA cm^{-2} (10–15 cycles), 160 mA cm^{-2} (16–20 cycles) and 40 mA cm^{-2} (21–25 cycles).

Table 1

The comparison of the electrochemical performances of VRFBs using various metal-free carbon based electrode materials

Electrode	Area (cm^2)	Current density (mA cm^{-2})	CE%	VE%	EE%	Ref
N-TCC	6	40	96.16	94.07	90.47	This work
		80	97.67	88.78	86.71	
		120	98.12	82.96	81.4	
		160	98.14	79.07	77.6	
N ₂ O co-doped GF	4	50	95	82	78	[31]
N-CNT/GF	9	50	97	90.7	88	[32]
B ₄ C/GF	4	160		82	80	[33]
boron-doped/GF	4	160	97	90	87.4	[34]
P-doped/GF	25	150	96	82	78.7	[35]
EGF	16	100	97	83.4	80.2	[36]
G/CF	9	100	-	-	76	[37]
Carbon NPs/GF	4.68	100	77.1	91	84.8	[38]
NCF/CF	4	320	86	85.1	85.1	[39]
rGO-GF	4	200	96.6	74.5	72	[40]
CPC	12	140	94.7	82.4	78.1	[41]

the carbon fiber network. Fig. 4b-d shows the energy efficiency (EE), coulombic efficiency (CE) and voltage efficiency (VE) of the cells with N-TCC, TCC and bare GF at current densities from 40 to 160 mA cm^{-2} . As

expected, while increasing the current density its efficiencies were rapidly decreased for bare GF (EE of 87.7% to 71.2% and VE of 92.22% to 72.9%) which listed in Table S2. In contrast, N-TCC and TCC cells were operated quite normally at current densities from 40 to 160 mA cm^{-2} , which showed the initial EE and VE of 90.47% and 77.6% and finalized as EE and VE of 90.47% and 76.02%. Among the as-constructed VRFB cells, the VRFB cell constructed with N-TCC exhibits a higher voltage efficiency (79.07%) at a current density of 160 mA cm^{-2} than TCC-cell (77.29%) and bare GF-cell (72.96%) as shown in Fig. 4b.

Moreover, N-TCC cell exhibited the energy efficiency of 77.6% at a current density of 160 mA cm^{-2} , while TCC and GF showed a lower energy efficiency of 76% and 71.2%, respectively. Hence, the obtained electrochemical performance of the full cell results reveals that the nitrogen doped carbon cloth (N-TCC) is surpassing the as-constructed TCC and bare GF cells attributed to the enhanced redox reaction kinetics of $\text{VO}^{2+}/\text{VO}_2^{+}$ and $\text{V}^{2+}/\text{V}^{3+}$ redox couples. Also, the obtained results of N-TCC based VRFBs are highly comparable with several reports available on carbon based redox flow batteries as summarized in Table 1. The cyclability tests showing that there is obvious enhancement during the charge-discharge cycles while using the as-prepared flexible electrodes. As shown in Fig. 5, NTCC sample keep excellent GCD profiles for all cycles while TCC electrode slightly start to deviate when compared to NTCC, while highly deviated with only GF electrodes. These findings suggests the surface functional groups can effectively improve the electrochemical activity to increase their capacity of the flow battery.

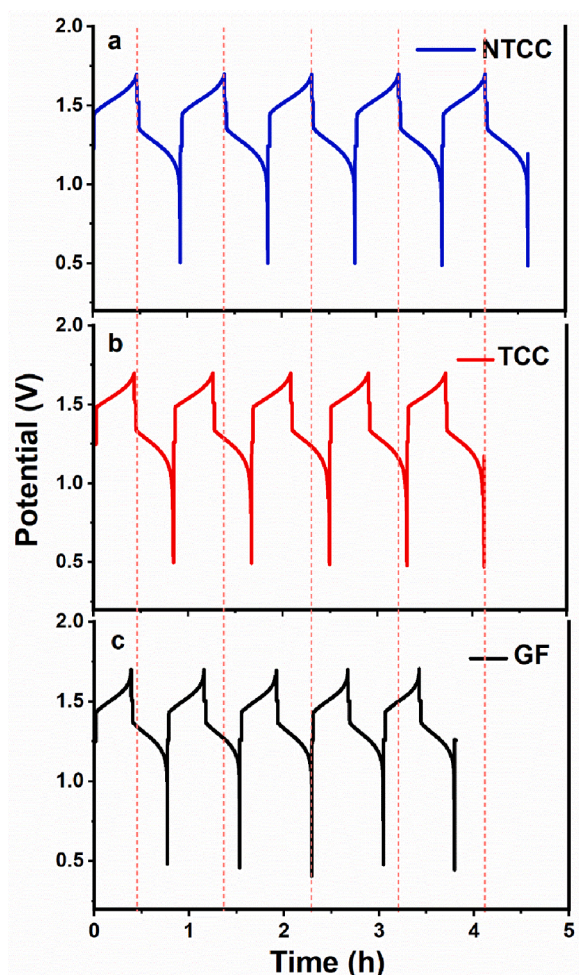


Fig. 5. Cyclability tests showing the variations observed within the 5 first cycles for: a) NTCC, b) TCC, c) GF.

4. Conclusion

The nitrogen doped carbon cloth has successfully derived from Terry cloth towel and have utilized for the first time in VRFBs as flexible electrodes. Notably, we achieved a well-defined redox peaks for electrocatalytic reactions of vanadium species with a lower over oxidation and reduction peaks. And the obtained half-cell electrochemical parameters are highly surpassing several reports on carbon based electrodes towards vanadium species. The key point of the conversion of cellulose fibers into carbon fibers lies in the terms of sustainable, from waste to energy, direct conversion of fiber structures, mechanically flexible, and high oxygen content with multi pore channels. These characteristics of the carbon cloth electrodes will offer to achieve high energy efficiency, voltage efficiency, and columbic efficiency and this can be a green solution for the textile based energy storage devices. These findings suggest us to find low-cost, more sustainable, and high performance electrodes which mainly alternatives to the fossil based carbon-fiber electrodes.

Credit authorship contribution statement

Rajesh Madhu: Performed Experiments

Supplementary Information

Supplementary data to this article can be found online at <https://XXXXXXXXXX>

CRediT authorship contribution statement

Rajesh Madhu: Conceptualization, Investigation, Validation, Data curation, Formal analysis, Methodology, Project administration, Supervision, Writing – original draft, Writing – review & editing. **Fedor V Kusmartsev:** Data curation, Funding acquisition, Writing – review & editing. **Kue-ho Kim:** Data curation. **Hyo-Jin Ahn:** Funding acquisition, Project administration, Supervision.

Declaration of competing interest

The authors declare NO competing financial interests.

Data Availability

Data will be made available on request.

Acknowledgement

The authors R.M and F.V.K grateful for the financial support from 985 FSU-2021-030/8474000371, Khalifa University, Abu Dhabi, UAE and the EU H2020 RISE project TERAASSE (H2020-823878). The authors K-H.K and H-J.A thankful to financial support from Seoul National University of Science and Technology, Seoul, South Korea.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:[10.1016/j.electacta.2022.141619](https://doi.org/10.1016/j.electacta.2022.141619).

References

- [1] J. Winsberg, T. Hagemann, T. Janoschka, M.D. Hager, U.S. Schubert, Redox-Flow Batteries: From Metals to Organic Redox-Active Materials, *Angew. Chemie Int. Ed.* 56 (2017) 686–711, <https://doi.org/10.1002/anie.201604925>.
- [2] L. Joerissen, J. Garche, C. Fabjan, G. Tomazic, Possible use of vanadium redox-flow batteries for energy storage in small grids and stand-alone photovoltaic systems, *J. Power Sources*. 127 (2004) 98–104, <https://doi.org/10.1016/j.jpowsour.2003.09.066>.
- [3] A.R. Landgrebe, S.W. Donley, Battery storage in residential applications of energy from photovoltaic sources, *Appl. Energy*. 15 (1983) 127–137, [https://doi.org/10.1016/0306-2619\(83\)90039-9](https://doi.org/10.1016/0306-2619(83)90039-9).
- [4] R. Shah, N. Mithulananthan, R.C. Bansal, Damping performance analysis of battery energy storage system, ultracapacitor and shunt capacitor with large-scale photovoltaic plants, *Appl. Energy*. 96 (2012) 235–244, <https://doi.org/10.1016/j.apenergy.2011.09.035>.
- [5] C. Choi, S. Kim, R. Kim, Y. Choi, S. Kim, H. Jung, J.H. Yang, H.-T. Kim, A review of vanadium electrolytes for vanadium redox flow batteries, *Renew. Sustain. Energy Rev.* 69 (2017) 263–274, <https://doi.org/10.1016/j.rser.2016.11.188>.
- [6] S. Kim, J. Yan, B. Schwenzer, J. Zhang, L. Li, J. Liu, Z.(Gary) Yang, M.A. Hickner, Cycling performance and efficiency of sulfonated poly(sulfone) membranes in vanadium redox flow batteries, *Electrochem. Commun.* 12 (2010) 1650–1653, <https://doi.org/10.1016/j.elecom.2010.09.018>.
- [7] C. Sun, J. Chen, H. Zhang, X. Han, Q. Luo, Investigations on transfer of water and vanadium ions across Nafion membrane in an operating vanadium redox flow battery, *J. Power Sources*. 195 (2010) 890–897, <https://doi.org/10.1016/j.jpowsour.2009.08.041>.
- [8] W.D. CAO Liuyue, SKYLLAS-KAZACOS Maria, Electrode modification and electrocatalysis for redox flow battery (RFB) applications, *Energy Storage, Sci. Technol.* 4 (2015) 433e457, <https://doi.org/10.3969/j.issn.2095-4239.2015.05.001>.
- [9] M. Skyllas-Kazacos, L. Cao, M. Kazacos, N. Kausar, A. Mousa, Vanadium Electrolyte Studies for the Vanadium Redox Battery-A Review, *ChemSusChem* 9 (2016) 1521–1543, <https://doi.org/10.1002/cssc.201600102>.
- [10] Z.H. Zhang, T.S. Zhao, B.F. Bai, L. Zeng, L. Wei, A highly active biomass-derived electrode for all vanadium redox flow batteries, *Electrochim. Acta*. 248 (2017) 197–205, <https://doi.org/10.1016/j.electacta.2017.07.129>.
- [11] G. Hu, M. Jing, D.-W. Wang, Z. Sun, C. Xu, W. Ren, H.-M. Cheng, C. Yan, X. Fan, F. Li, A gradient bi-functional graphene-based modified electrode for vanadium redox flow batteries, *Energy Storage Mater* 13 (2018) 66–71, <https://doi.org/10.1016/j.ensm.2017.12.026>.
- [12] B.R. Chalamala, T. Soundappan, G.R. Fisher, M.R. Anstey, V.V. Viswanathan, M. L. Perry, Redox Flow Batteries: An Engineering Perspective, *Proc. IEEE* 102 (2014) 976–999, <https://doi.org/10.1109/JPROC.2014.2320317>.

- [13] P. Schlee, S. Herou, R. Jervis, P.R. Shearing, D.J.L. Brett, D. Baker, O. Hosseinaei, P. Tomani, M.M. Murshed, Y. Li, M.J. Mostazo-López, D. Cazorla-Amorós, A. B. Jorge Sobrido, M.-M. Titirici, Free-standing supercapacitors from Kraft lignin nanofibers with remarkable volumetric energy density, *Chem. Sci.* 10 (2019) 2980–2988, <https://doi.org/10.1039/C8SC04936J>.
- [14] G. Wei, X. Fan, J. Liu, C. Yan, A review of the electrochemical activity of carbon materials in vanadium redox flow batteries, *Carbon N. Y.* 81 (2015) 850, <https://doi.org/10.1016/j.carbon.2014.08.032>.
- [15] M.C. Ribadeneyra, L. Grogan, H. Au, P. Schlee, S. Herou, T. Neville, P.L. Cullen, M. D.R. Kok, O. Hosseinaei, S. Danielsson, P. Tomani, M.M. Titirici, D.J.L. Brett, P. R. Shearing, R. Jervis, A.B. Jorge, Lignin-derived electrospun freestanding carbons as alternative electrodes for redox flow batteries, *Carbon N. Y.* 157 (2020) 847–856, <https://doi.org/10.1016/j.carbon.2019.11.015>.
- [16] A.G. Avila, J.P. Hinestroza, Tough cotton, *Nat. Nanotechnol.* 3 (2008) 458–459, <https://doi.org/10.1038/nnano.2008.233>.
- [17] R.F. Service, Electronic Textiles Charge Ahead, *Science* (80-.). 301 (2003) 909–911, <https://doi.org/10.1126/science.301.5635.909>.
- [18] C. Zhong, Y. Deng, W. Hu, J. Qiao, L. Zhang, J. Zhang, A review of electrolyte materials and compositions for electrochemical supercapacitors, *Chem. Soc. Rev.* 44 (2015) 7484–7539, <https://doi.org/10.1039/C5CS00303B>.
- [19] P. Dai, S. Zhang, H. Liu, L. Yan, X. Gu, L. Li, D. Liu, X. Zhao, Cotton fabrics-derived flexible nitrogen-doped activated carbon cloth for high-performance supercapacitors in organic electrolyte, *Electrochim. Acta.* 354 (2020), 136717, <https://doi.org/10.1016/j.electacta.2020.136717>.
- [20] L. Bao, X. Li, Towards Textile Energy Storage from Cotton T-Shirts, *Adv. Mater.* 24 (2012) 3246–3252, <https://doi.org/10.1002/adma.201200246>.
- [21] L. Chen, T. Ji, L. Mu, J. Zhu, Cotton fabric derived hierarchically porous carbon and nitrogen doping for sustainable capacitor electrode, *Carbon N. Y.* 111 (2017) 839–848, <https://doi.org/10.1016/j.carbon.2016.10.054>.
- [22] J. Bae, M.K. Song, Y.J. Park, J.M. Kim, M. Liu, Z.L. Wang, Fiber Supercapacitors Made of Nanowire-Fiber Hybrid Structures for Wearable/Flexible Energy Storage, *Angew. Chemie Int. Ed.* 50 (2011) 1683–1687, <https://doi.org/10.1002/anie.201006062>.
- [23] G. Yu, L. Hu, M. Vosgueritchian, H. Wang, X. Xie, J.R. McDonough, X. Cui, Y. Cui, Z. Bao, Solution-Processed Graphene/MnO₂ Nanostructured Textiles for High-Performance Electrochemical Capacitors, *Nano Lett* 11 (2011) 2905–2911, <https://doi.org/10.1021/nl2013828>.
- [24] C. Yuan, L. Hou, D. Li, L. Shen, F. Zhang, X. Zhang, Synthesis of flexible and porous cobalt hydroxide/conductive cotton textile sheet and its application in electrochemical capacitors, *Electrochim. Acta.* 56 (2011) 6683–6687, <https://doi.org/10.1016/j.electacta.2011.05.050>.
- [25] J. Wu, C. Jin, Z. Yang, J. Tian, R. Yang, Synthesis of phosphorus-doped carbon hollow spheres as efficient metal-free electrocatalysts for oxygen reduction, *Carbon N. Y.* 82 (2015) 562–571, <https://doi.org/10.1016/j.carbon.2014.11.008>.
- [26] F. Su, C.K. Poh, J.S. Chen, G. Xu, D. Wang, Q. Li, J. Lin, X.W. Lou, Nitrogen-containing microporous carbon nanospheres with improved capacitive properties, *Energy Environ. Sci.* 4 (2011) 717–724, <https://doi.org/10.1039/C0EE00277A>.
- [27] J. Xu, Y. Zhang, Z. Huang, C. Jia, S. Wang, Surface Modification of Carbon-Based Electrodes for Vanadium Redox Flow Batteries, *Energy & Fuels* 35 (2021) 8617–8633, <https://doi.org/10.1021/acs.energyfuels.1c00722>.
- [28] A. Fetyan, J. Schneider, M. Schnucklake, G.A. El-Nagar, R. Banerjee, N. Bevilacqua, R. Zeis, C. Roth, Comparison of Electrospun Carbon–Carbon Composite and Commercial Felt for Their Activity and Electrolyte Utilization in Vanadium Redox Flow Batteries, *ChemElectroChem* 6 (2019) 130–135, <https://doi.org/10.1002/celec.201801128>.
- [29] A. Fetyan, I. Derr, M.K. Kayarkatte, J. Langner, D. Bernsmeier, R. Kraehnert, C. Roth, Electrospun Carbon Nanofibers as Alternative Electrode Materials for Vanadium Redox Flow Batteries, *ChemElectroChem* 2 (2015) 2055–2060, <https://doi.org/10.1002/celec.201500284>.
- [30] M. Ulaganathan, A. Jain, V. Aravindan, S. Jayaraman, W.C. Ling, T.M. Lim, M. P. Srinivasan, Q. Yan, S. Madhavi, Bio-mass derived mesoporous carbon as superior electrode in all vanadium redox flow battery with multicouple reactions, *J. Power Sources.* 274 (2015) 846–850, <https://doi.org/10.1016/j.jpowsour.2014.10.176>.
- [31] Y. Huang, Q. Deng, X. Wu, S. Wang, N. O Co-doped carbon felt for high-performance all-vanadium redox flow battery, *Int. J. Hydrogen Energy.* 42 (2017) 7177–7185, <https://doi.org/10.1016/j.ijhydene.2016.04.004>.
- [32] D.-S. Yang, J.Y. Lee, S.-W. Jo, S.J. Yoon, T.-H. Kim, Y.T. Hong, Electrocatalytic activity of nitrogen-doped CNT graphite felt hybrid for all-vanadium redox flow batteries, *Int. J. Hydrogen Energy.* 43 (2018) 1516–1522, <https://doi.org/10.1016/j.ijhydene.2017.11.145>.
- [33] H.R. Jiang, W. Shyy, M.C. Wu, L. Wei, T.S. Zhao, Highly active, bi-functional and metal-free B 4 C-nanoparticle-modified graphite felt electrodes for vanadium redox flow batteries, *J. Power Sources.* 365 (2017) 34–42, <https://doi.org/10.1016/j.jpowsour.2017.08.075>.
- [34] H.R. Jiang, W. Shyy, L. Zeng, R.H. Zhang, T.S. Zhao, Highly efficient and ultra-stable boron-doped graphite felt electrodes for vanadium redox flow batteries, *J. Mater. Chem. A.* 6 (2018) 13244–13253, <https://doi.org/10.1039/C8TA03388A>.
- [35] L. Yu, F. Lin, L. Xu, J. Xi, P-doped electrode for vanadium flow battery with high-rate capability and all-climate adaptability, *J. Energy Chem.* 35 (2019) 55–59, <https://doi.org/10.1016/j.jechem.2018.11.004>.
- [36] J.J. Park, J.H. Park, O.O. Park, J.H. Yang, Highly porous graphenated graphite felt electrodes with catalytic defects for high-performance vanadium redox flow batteries produced via NiO/Ni redox reactions, *Carbon N. Y.* 110 (2016) 17–26, <https://doi.org/10.1016/j.carbon.2016.08.094>.
- [37] Z. González, C. Flox, C. Blanco, M. Granda, J.R. Morante, R. Menéndez, R. Santamaría, Outstanding electrochemical performance of a graphene-modified graphite felt for vanadium redox flow battery application, *J. Power Sources.* 338 (2017) 155–162, <https://doi.org/10.1016/j.jpowsour.2016.10.069>.
- [38] L. Wei, T.S. Zhao, G. Zhao, L. An, L. Zeng, A high-performance carbon nanoparticle-decorated graphite felt electrode for vanadium redox flow batteries, *Appl. Energy.* 176 (2016) 74–79, <https://doi.org/10.1016/j.apenergy.2016.05.048>.
- [39] X. Zhou, X. Zhang, Y. Lv, L. Lin, Q. Wu, Nano-catalytic layer engraved carbon felt via copper oxide etching for vanadium redox flow batteries, *Carbon N. Y.* 153 (2019) 674–681, <https://doi.org/10.1016/j.carbon.2019.07.072>.
- [40] Q. Deng, P. Huang, W.-X. Zhou, Q. Ma, N. Zhou, H. Xie, W. Ling, C.-J. Zhou, Y.-X. Yin, X.-W. Wu, X.-Y. Lu, Y.-G. Guo, A High-Performance Composite Electrode for Vanadium Redox Flow Batteries, *Adv. Energy Mater.* 7 (2017), 1700461, <https://doi.org/10.1002/aenm.201700461>.
- [41] T. Liu, X. Li, C. Xu, H. Zhang, Activated Carbon Fiber Paper Based Electrodes with High Electrochemical Activity for Vanadium Flow Batteries with Improved Power Density, *ACS Appl. Mater. Interfaces.* 9 (2017) 4626–4633, <https://doi.org/10.1021/acsami.6b14478>.