Electronic Supplementary Information

$NiMoO_4$ nanorods with rich catalytic sites as superb electrocatalyst for cerium-based flow battery

*Xian XIE, Chung Yim CHAN, and Walid A. DAOUD**

* School of Energy and Environment, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong. E-mail: wdaoud@cityu.edu.hk; Tel: +852-3442-4499

Table S1. Comparison of all-vanadium, zinc-bromine and cerium-based RFB

RFB	Redox reactions	Theoretical cell voltage (V)	Current density (mA cm^{-2})	Cost of electrolyte	
				Negative species (USD kg^{-1})	Positive species (USD kg^{-1})
All-vanadium	$VO_2^+ + 2H^+ + e^- \leftrightarrow VO^{2+} + H_2O$ $E^0 = 1.0$ V $V^{3+} + e^- \leftrightarrow V^{2+}$ $E^0 = -0.26$ V	1.26	80-200	24	24
Bromine-Zinc	$Br_2 + 2e^- \leftrightarrow 2Br$ $E^0 = 1.087$ V $Zn^{2+} + 2e^- \leftrightarrow Zn$ $E^0 = -0.76$ V	1.847	20-80	1.9	2.0
Cerium-Zinc	$Ce^{4+} + e^- \leftrightarrow Ce^{3+}$ $E^0 = 1.61$ V $Zn^{2+} + 2e^- \leftrightarrow Zn$ $E^0 = -0.76$ V	2.37	20-50	1.9	12
Cerium-Vanadium	$Ce^{4+} + e^- \leftrightarrow Ce^{3+}$ $E^0 = 1.61$ V $V^{3+} + e^- \leftrightarrow V^{2+}$ $E^0 = -0.26$ V	1.87	50-100	24	12

Table S2. Comparison of electrode modification approaches in all-vanadium RFB

Strategies	Approaches	Pros and cons
Introducing functional groups	Thermal treatment; Concentrated acid treatment; Electrochemical oxidation; Fenton's reagent treatment, etc.	Easy operation, limited performance, unsafe and not environmental friendly (for concentrated acid treatment)
Larger surface area	Nano-scaled carbon (graphene, graphene oxide, single/multi-walled carbon nanotubes) decorated GF; chemical etching, etc.	Boosting mass transfer; expensive (graphene: $ 1/mg, platinum: $ 0.0294/mg); roundabout and wasteful (for chemical etching)
Enhancing catalytic effect	Metal oxides deposition via hydrothermal reaction, impregnation, and electrochemical deposition, etc.	Show promising electrochemical performance, suffered from stability and scalability

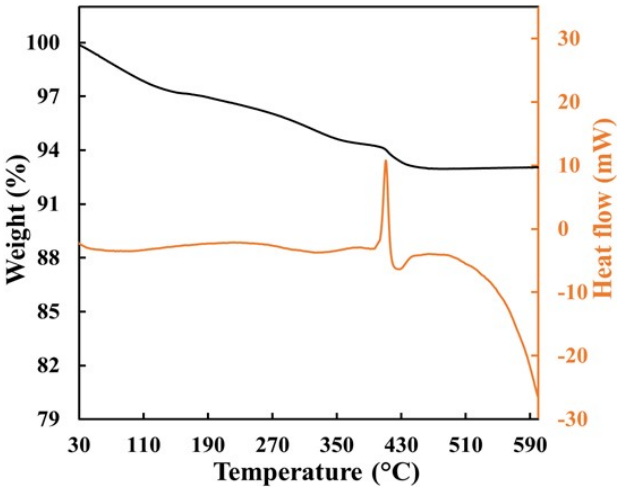


Fig. S1 TGA/DSC curve of $NiMoO_4 \bullet xH_2O$ precursor under N_2 environment

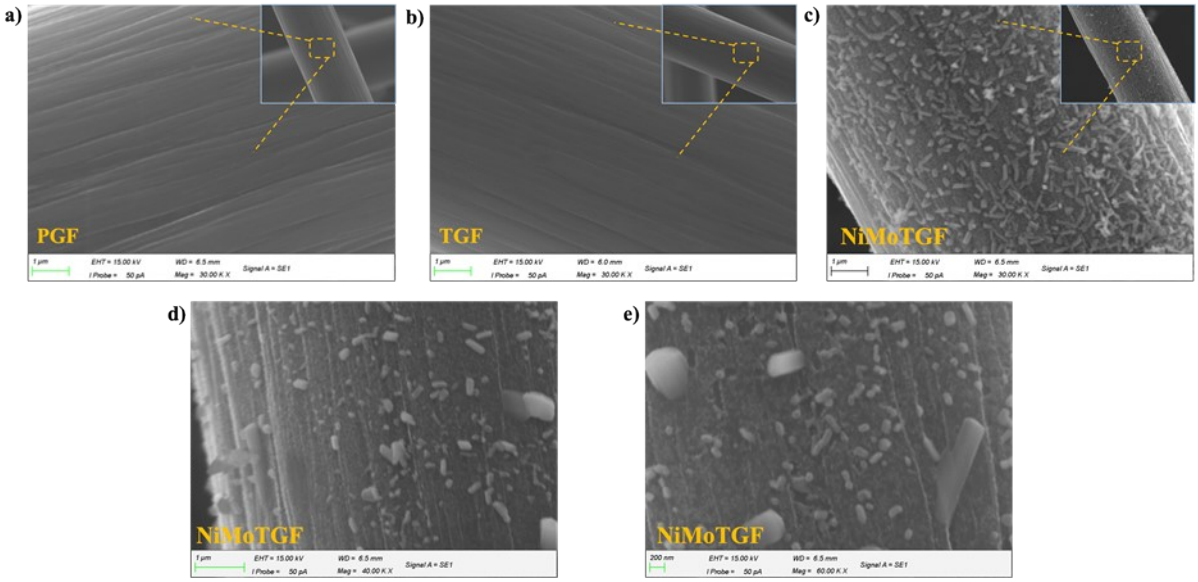


Fig. S2 SEM image of (a) PGF; (b) TGF at magnification of 30000; (c-e) NiMoTGF at magnification of 30000, 40000 and 60000, respectively

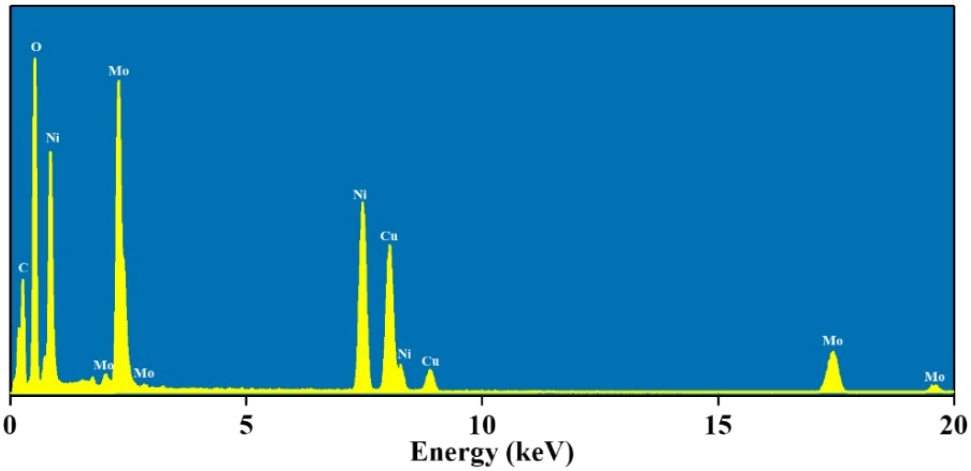
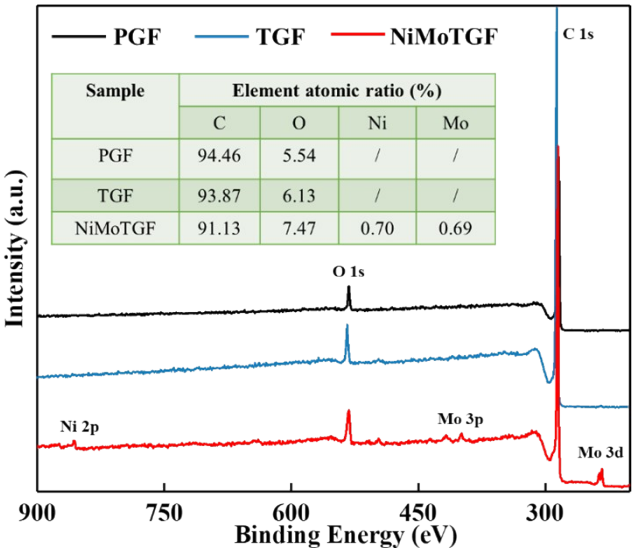


Fig. S3 HRTEM-EDS spectra of $NiMoO_4$ nanorod



Sample	Element atomic ratio (%)			
	C	O	Ni	Mo
PGF	94.46	5.54	/	/
TGF	93.87	6.13	/	/
NiMoTGF	91.13	7.47	0.70	0.69

Fig. S4 XPS survey of PGF, TGF and NiMoTGF

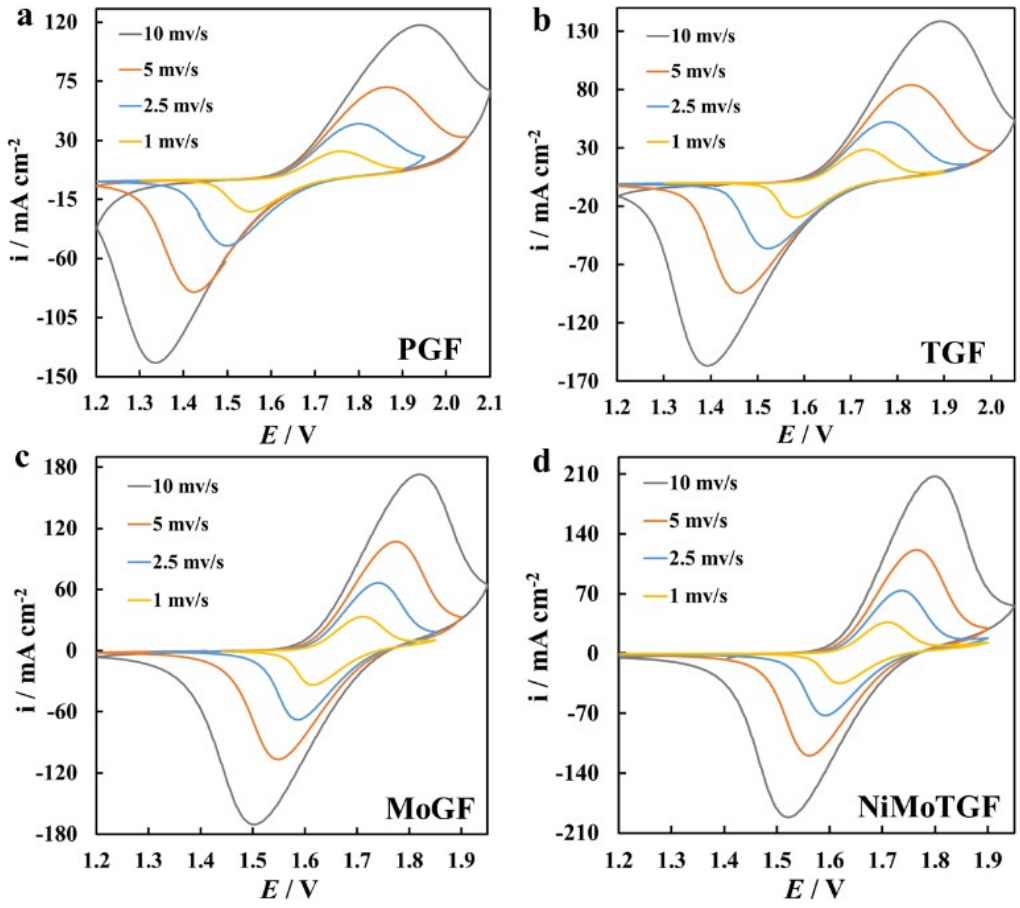


Fig. S5 CV profiles of (a) PGF; (b) TGF; (c) MoGF and (d) NiMoTGF at different scan rates

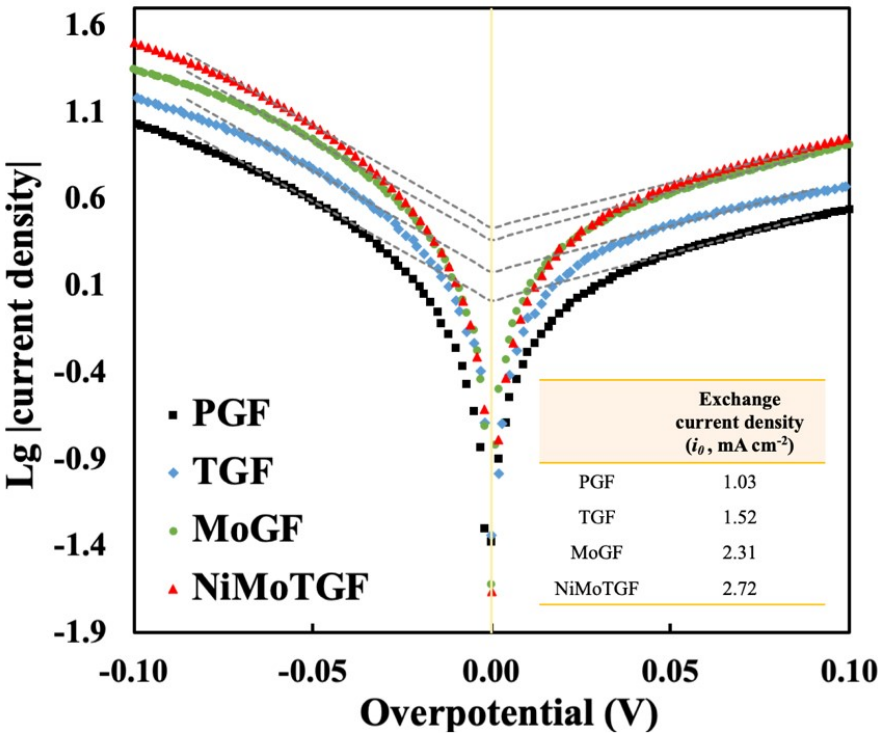


Fig. S6 Tafel plots of PGF, TGF, MoGF and NiMoTGF (derived from 1mv s^{-1} CV profiles)

The kinetics of the $Ce^{3+/}C3^{4+}$ reaction on graphite felt were analyzed using the Tafel equation:

$$\eta = \frac{2.3\ RT}{\alpha nF}\lg i_0 \pm \frac{2.3\ RT}{\alpha nF} lg|i|$$

where i is the current density, i_0 is the exchange current density, α is the symmetry factor, n is the number of transferred electrons, F is the Faraday constant, R is the universal gas constant and T is the temperature. In particular, for a one-step single-electron-transfer reaction, the sum of αc and αa must equal unity, $\alpha_c + \alpha_a = 1$, where αc and αa are the cathodic and anodic transfer coefficient, respectively. [1] The linear Tafel fitting was performed and i_0 was calculated using the Tafel equation by knowing the intercept and Tafel slope.

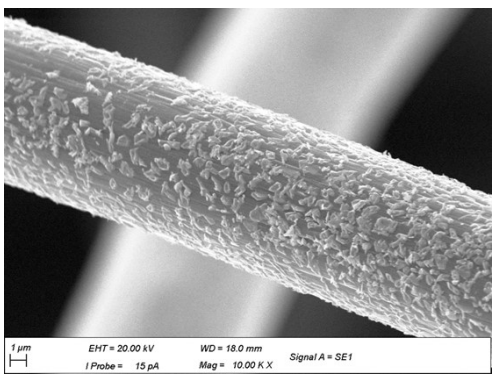


Fig. S7 SEM image of MoGF at magnification of 10000

Table S3. EIS fitting data acquired from EIS curves in **Fig. 7**

Sample	R_b (Ω)	CPE_1		R_{ct} (Ω)	CPE_2	
		V (F)	α		V (F)	α
PGF	0.52	0.78×10^{-3}	0.89	4.03	1.78	0.80
TGF	0.50	1.04×10^{-3}	0.89	1.83	1.39	0.76
NiMoTGF	0.48	1.23×10^{-3}	0.81	0.42	2.73	0.87

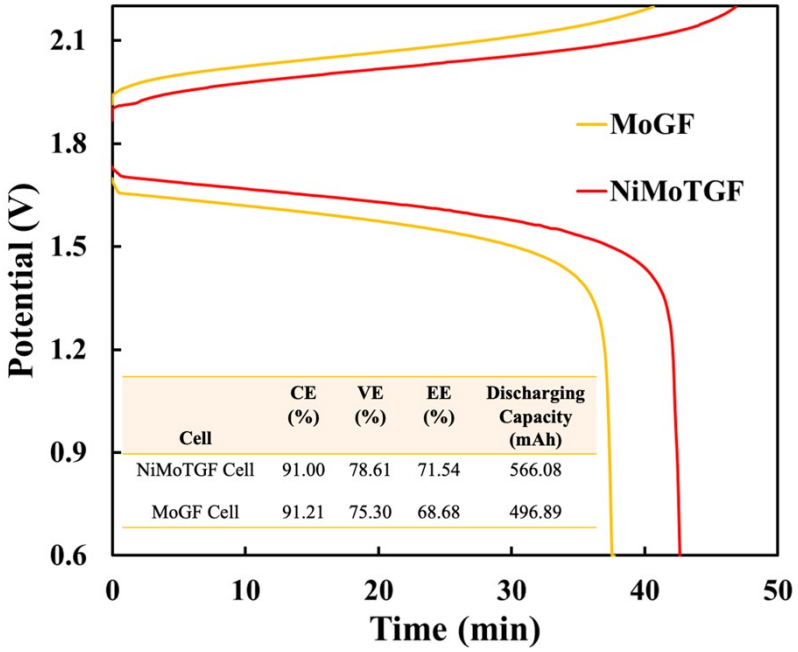


Fig. S8 Charge-discharge profiles and cell performance of MoGF and NiMoTGF cell

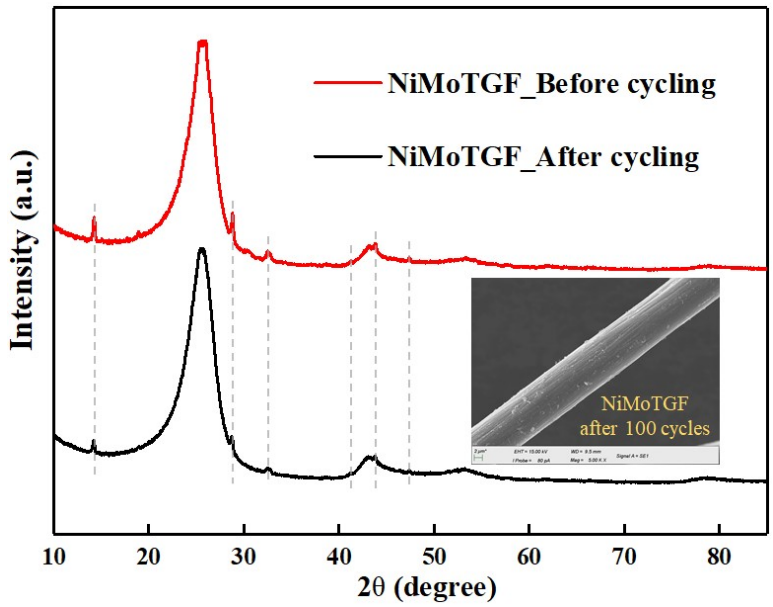


Fig. S9 XRD and SEM of NiMoTGF after 100 cycles

Table S4. Comparison of notable works on graphite felt electrode modification for cerium-based and all-vanadium flow batteries

Electrode material	Electrolyte (negative - positive)	Electrode preparation method	Membrane	Current density (mA cm^{-2})	VE (%)	Discharging capacity increase (%) [a]	Ref.
			Cerium-based flow battery				
SnO_2	1.5 M Pb(II) - 0.5 M Ce(III), both in 1 M CH_4O_3S	Concentrated acid treatment, hydrothermal, calcination	GEFC-104	30 *	71.5	- (40 mAh fix capacity charging)	2
Metal-organic framework	1.5 M Pb(II) - 1 M Ce(III), both in 1 M CH_4O_3S	Impregnation, calcination, concentrated acid treatment	GEFC-104	30 *	68.5	- (40 mAh fix capacity charging)	3
			All-vanadium flow battery				
Nitrogen-carbon nanospheres	0.75 M V(III) + 0.75 M V(IV) in 2 M H_2SO_4 (both positive and negative electrolyte)	Polymerization, carbonization (900 °C, 2h)	Nafion 115	150 200 300 *	77 69.8 55.5	21.6 79.6 -	4
Reduced graphene oxide	0.75 M V(III) + 0.375 M V(IV) in 3 M H_2SO_4 (both positive and negative electrolyte)	Chemical activation, hydrothermal	Nafion 115	150 200 300 *	81 74.5 63	285.5 - -	5
Surface exfoliation	1.5 M V(III) – 1.5 M V(IV), both in 3 M H_2SO_4	Electrochemical exfoliation at 10 V	Nafion 115	150 200 *	74.4 61	63.5 32.13	6
Surface wrinkle	1.5 M V(III) – 1.5 M V(IV), both in 3 M H_2SO_4	Hydrothermal, calcination	Nafion 115	150 200 300 *	78.5 72.5 59.8	33.3 - -	7
NiO	2 M V(III) - 2 M V(IV), both in 3 M H_2SO_4	Impregnation, calcination	Nafion 117	125 150 *	77.5 72.5	62.2 -	8
$NiCoO_2$	2 M V(III) - 2 M V(IV), both in 2.5 M H_2SO_4	Hydrothermal, calcination	GN-114C	150 *	81.2	153.2	9
$CeZrO_2$	2 M V(III) - 2 M V(IV), both in 2 M H_2SO_4	Hydrothermal, calcination	Nafion 115	150 200 300 *	77.8 71.5 58.5	42.1 - -	10
MoO_3	1.2 M V(III) – 1.2 M V(IV), both in 2.5 M H_2SO_4	Impregnation, calcination	Nafion 117	150 200 250 *	81.0 76.1 71.4	139.7 - -	11
ZrO_2 metal-organic framwork	0.8 M V(III) – 0.8 M V(IV), both in 3 M H_2SO_4	Hydrothermal, calcination	Nafion 115	150 200 300 *	83 77.5 62.4	40 207 -	12
			Cerium-vanadium flow battery				
$NiMoO_4$	1 M V(III) in 5.5 M CH_4O_3S – 1 M Ce(III) in 3.5 M CH_4O_3S	Hydrothermal, calcination	Nafion 212	150 200 300 *	81.93 77.17 70.03	50.64 - -	This work

a. Discharging capacity increase over pristine graphite felt

* Highest current density reported

Reference

1. A. Heinritz, T. Binninger, A. Patru and T. J. Schmidt, *ACS Catal*, 2021, **11**, 8140-8154.
2. Z. Na, X. Wang, D. Yin and L. Wang, *J. Mater. Chem. A*, 2017, **5**, 5036-5043.
3. Z. Na, R. Yao, Q. Yan, X. Wang, G. Huang and X. Sun, *Energy Stor. Mater*. 2020, **32**, 11-19.
4. L. Wu, Y. Shen, L. Yu, J. Xi and X. Qiu, *Nano Energy*, 2016, **28**, 19-28.
5. 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 and Y.-G. Guo, *Adv. Energy Mater.* 2017, **7**.
6. A. Mukhopadhyay, Y. Yang, Y. Li, Y. Chen, H. Li, A. Natan, Y. Liu, D. Cao and H. Zhu, *Adv. Funct. Mater.* 2019, **29**, 1903192.
7. Z. Chen, Y. Gao, C. Zhang, X. Zeng and X. Wu, *Adv. Electron. Mater.* 2019, **5**.
8. N. Yun, J. J. Park, O. O. Park, K. B. Lee and J. H. Yang, *Electrochim. Acta*, 2018, **278**, 226-235.
9. Y. Xiang and W. A. Daoud, *J. Mater. Chem. A*, 2019, **7**, 5589-5600.
10. L. Yu, F. Lin, W. Xiao, L. Xu and J. Xi, *Chem. Eng. J.* 2019, **356**, 622-631.
11. X. Xie, Y. Xiang and W. A. Daoud, *ACS Appl. Energy Mater.* 2020, **3**, 10463-10476.
12. Y. Jiang, G. Cheng, Y. Li, Z. He, J. Zhu, W. Meng, L. Dai and L. Wang, *Chem. Eng. J.* 2021, **415**, 129014.