

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

COMMUNICATION

RuSe/reduced graphene oxide: an efficient electrocatalyst for $\text{VO}^{2+}/\text{VO}_2^+$ redox couples in vanadium redox flow batteries

Cite this: DOI: 10.1039/x0xx00000x

Received 00th February 2014,

DOI: 10.1039/x0xx00000x

www.rsc.org/

Pengxian Han^{†a}, Xiaogang Wang^{†a}, Lixue Zhang,^a Tianshi Wang,^a Jianhua Yao,^a Changshui Huang,^a Lin Gu,^b and Guanglei Cui^{*a}

Selenium modified ruthenium/reduced graphene oxide (RuSe/rGO) is explored as an electrocatalyst towards $\text{VO}^{2+}/\text{VO}_2^+$ redox couples in vanadium redox flow batteries. Compared with rGO electrode, the RuSe/rGO can significantly alleviate the polarization and improve the reversibility of the redox reaction, by virtue of the excellent catalytic activity and electronic conductivity.

As one of the rechargeable energy storage devices, vanadium redox flow batteries (VRFBs) employ vanadium ions in different oxidation states to store chemical potential energy. Since the invention by Maria Skyllas-Kazacos and colleagues in the 1980s, it has received considerable attention due to the almost unlimited capacity and long cycle life.¹⁻³ However, one of the critical challenges of VRFBs is the relatively sluggish reaction kinetics of $\text{VO}^{2+}/\text{VO}_2^+$ redox couples.⁴ Since highly active electrocatalysts can effectively improve the kinetics of the redox couples, numerous efforts have been made to explore high performance electrocatalysts for VRFBs.⁵⁻⁸

It is reported that chalcogenide elements (S, Se and Te) can effectively modify the surface reactivity of some metal catalysts (Ru, Co, Fe, and Ni) and thus modulate their catalytic activity.^{9,10} Recently, chalcogenide-modified metal M_xX_y ($\text{M} = \text{Ru}, \text{Co}, \text{Fe}$ and Ni ; $\text{X} = \text{S}, \text{Se}$ and Te) become a very promising catalyst candidate towards some electrochemical reactions (e.g., oxygen reduction reaction, methanol oxidation reaction, etc.) because of their comparable catalytic activity, low cost, high abundance.¹¹⁻¹³ However, chalcogenide-modified metal electrocatalyst towards $\text{VO}^{2+}/\text{VO}_2^+$ couples for VRFBs has rarely been reported to the best of our knowledge.

In this communication, selenium modified ruthenium/reduced graphene oxide (RuSe/rGO) nanocomposite was explored as an electrocatalyst in VRFBs (see EIS for experimental details). It is manifested that RuSe/rGO nanocomposite can significantly alleviate the polarization and improve the reversibility of $\text{VO}^{2+}/\text{VO}_2^+$ redox couples. This enhanced performance should be attributed to the intrinsically high catalytic activity of RuSe and the good electronic conductivity of the composite endowed by rGO.^{14,15}

As shown in Fig. 1a, The X-ray diffraction (XRD) pattern of the prepared RuSe/rGO nanocomposite displays well-defined peaks, which are well accordance with the previous report, confirming the

formation of selenium modified ruthenium material.¹³ From the X-ray photoelectron spectroscopy (XPS) data (Fig. 2b), the surface element atom contents of the RuSe/rGO nanocomposite are calculated to be 78.96% carbon, 18.89% oxygen, 0.88% Ru and 0.36% Se, respectively. The transmission electron microscopy (TEM) and high resolution TEM images exhibit typical morphologies of the RuSe/rGO nanocomposite, showing that RuSe nanoparticles with an average diameter of 4 ± 0.5 nm are homogeneously anchored to the rGO surface (Fig. 1c, d), and this specific nanostructure may be beneficial to improve electrocatalytic activity.

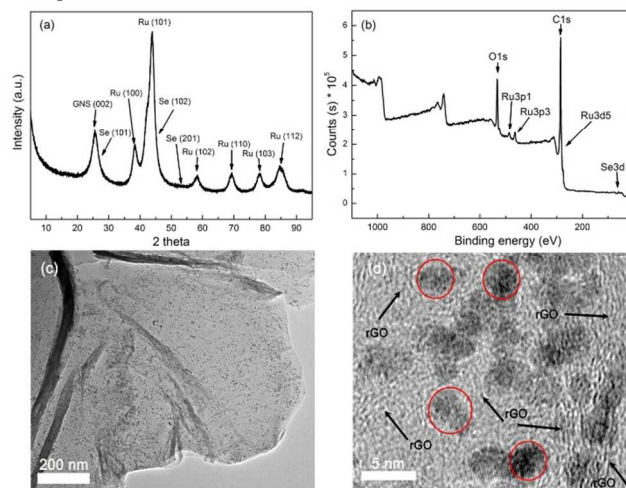


Fig. 1 (a) XRD pattern, (b) XPS general spectrum, (c) TEM image and (d) high resolution TEM image of RuSe/rGO nanocomposite, some RuSe nanoparticles are circled by red.

Fig. 2 depicts the elemental mappings of RuSe/rGO nanocomposite, it can be obviously seen that Se element incorporated with Ru element are homogeneously distributed throughout the rGO sheets. These results indicate that RuSe phase in RuSe/rGO nanocomposite is well dispersed. It could be expected that such a well-constructed texture may be favourable for the electrocatalytic redox reaction of $\text{VO}^{2+}/\text{VO}_2^+$ couples.¹³

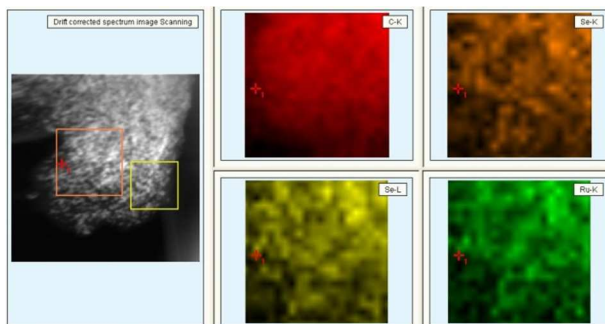


Fig. 2 Elemental mappings of RuSe/rGO nanocomposite.

As shown in Fig. 3a, the anodic and cathodic peak potential separation of $\text{VO}_2^+/\text{VO}_2^+$ redox couples at rGO modified electrode is 0.29 V at the scan rate of 2 mV s^{-1} and reaches to 0.50 V at the scan rate of 20 mV s^{-1} . In case of the RuSe/rGO modified electrode (Fig. 3b), the peak potential separation is just 0.17 V even though the scan rate reaches to 20 mV s^{-1} , demonstrating an alleviated polarization of $\text{VO}_2^+/\text{VO}_2^+$ redox couples at RuSe/rGO modified electrode. In addition, the anodic and cathodic peak current densities at RuSe/rGO modified electrode are much larger than that at rGO modified electrode. Another important factor related to redox reversibility is the ratio of peak current densities of the oxidation peak to the reduction peak ($|I_{pa}/I_{pc}|$).¹⁶ The peak current densities of $\text{VO}_2^+/\text{VO}_2^+$ redox couples under different scan rates are listed in Table S1. It can be seen from Table S1 that the values of $|I_{pa}/I_{pc}|$ for RuSe/rGO modified electrode are much smaller than that of rGO, indicating that RuSe/rGO presents much reversible electrocatalytic activity towards $\text{VO}_2^+/\text{VO}_2^+$ redox couples than rGO. Fig. S1 plots the Tafel polarization curve of rGO and RuSe/rGO. According to the Butler-Volmer equation, the calculated exchange current densities for rGO and RuSe/rGO are 5.62×10^{-5} and $1.12 \times 10^{-3} \text{ A cm}^{-2}$, respectively, further suggesting that RuSe/rGO modified electrode exhibits much better electrocatalytic performance. The alleviated potential separation, the enhanced peak current densities and exchange current density indicate more favorable electron transfer kinetics for $\text{VO}_2^+/\text{VO}_2^+$ redox reaction at RuSe/rGO modified electrode.¹⁷⁻¹⁹ The CV profiles of $\text{VO}_2^+/\text{VO}_2^+$ redox couples at RuSe/rGO modified electrode keep almost unchanged even after 300 cycles, indicating very good chemical durability of RuSe/rGO nanocomposite in acid electrolyte (Fig. 3c).

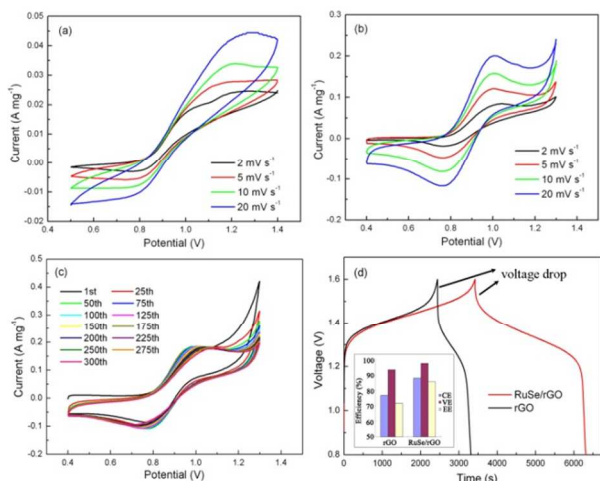


Fig. 3 CV curves of (a) rGO and (b) RuSe/rGO under different scan rates; (c) 300 cycles of RuSe/rGO; (d) charge-discharge curves at the current density of 20 mA cm^{-2} in the voltage range of 0.8-1.6 V (the inset in d is the CE, VE and EE of the cell).

Fig. 3d presents the charge-discharge curves of the constructed VRFB cells. It can be seen that the anchoring of RuSe on rGO surface significantly improves the performance compared with the rGO, possibly attributing to the synergistic catalytic effect between the nanosized RuSe and rGO. The RuSe/rGO electrode presents an alleviated voltage drop of 0.05 V in comparison with that of 0.11 V for rGO electrode. The coulombic efficiency (CE), voltage efficiency (VE), and overall energy efficiency (EE) of the RuSe/rGO-based VRFB cell are 87.9%, 97.3% and 85.5%, respectively, which is correspondingly superior to that of rGO-based cell (76.8%, 93.2% and 71.6%, respectively), exhibiting a significantly improved electrocatalytic effect of RuSe/rGO nanocomposite.

EIS was employed to further characterize the electrochemical processes of the samples. EIS data was recorded in $2 \text{ mol L}^{-1} \text{ VOSO}_4/2 \text{ mol L}^{-1} (\text{VO}_2)_2\text{SO}_4$ solution at the apparent standard potential. Fig. 4a and b display a sequence of characteristic Nyquist plots, in which the semicircle is attributed to a parallel combination of the charge transfer resistance with the double layer capacitance, and the sloped line is related to mass transport effects.^{20,21} The inset in Fig. 4a shows the equivalent circuit used for fitting. In the equivalent circuit, R_1 stands for the resistance composed of solution resistance, electrode resistance and the contact resistance. R_2 represents the charge transfer resistance across electrode/solution interface, Q_m (CPE1) is the constant-phase element which represents the electric double-layer capacitance of electrode/solution interface, and Q_t (CPE2) is the constant-phase element which represents the diffusion capacitance attributed by the diffusion process of VO_2^+ and VO_2^+ ions. Table 1 shows the fitted values from the EIS data. With regard to RuSe/rGO electrode, R_2 is only 5.3Ω

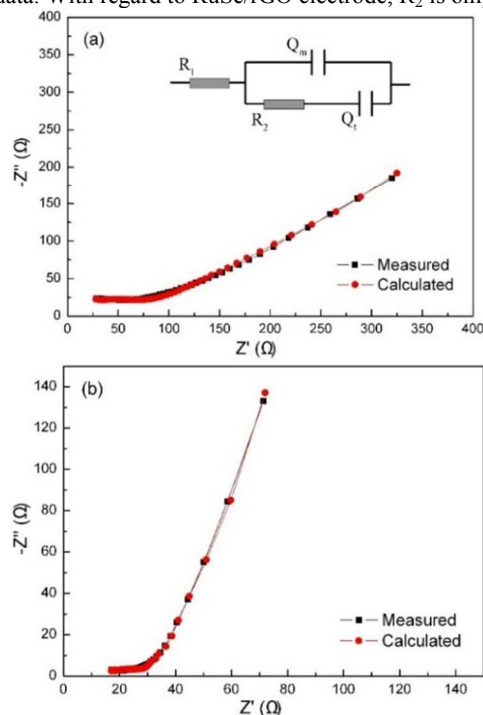


Fig. 4 Nyquist plots of the electrodes at the apparent standard potential: (a) rGO and (b) RuSe/rGO; The inset in (a) is the equivalent circuit.

for RuSe/rGO electrode, which is much smaller than that of 87.6Ω for rGO electrode. From Table 1, it also can be seen that the values of Q_m and Q_t for RuSe/rGO electrode are higher than that of rGO electrode, indicating an enhancement of the electric double-layer capacitance of electrode/electrolyte interface and the diffusion

capacitance of ions. The former favors the charge transfer for the $\text{VO}^{2+}/\text{VO}_2^+$ redox reaction and the latter is beneficial for the diffusion of VO^{2+} and VO_2^+ ions towards the composite electrode.²² The RuSe/rGO nanocomposite is favorable to the ion and electron transport, so the polarization is dramatically alleviated and the reversibility is significantly improved.

Table 1 Parameters resulted from fitting the Nyquist plots.

Sample	$R_1(\Omega)$	$Q_m(\text{CPE}_1)$	$R_2(\Omega)$	$Q_t(\text{CPE}_2) \times 10^{-2}$
rGO	12.3 ± 0.2	3.5 ± 0.04 × 10 ⁻⁶	87.6 ± 0.6	1.6 ± 0.08 × 10 ⁻³
RuSe/rGO	9.1 ± 0.1	1.4 ± 0.02 × 10 ⁻⁴	5.3 ± 0.2	5.3 ± 0.11 × 10 ⁻³

In summary, the RuSe/rGO nanocomposite was prepared and explored as a novel electrocatalyst towards $\text{VO}^{2+}/\text{VO}_2^+$ redox couples in VRFBs. RuSe/rGO modified electrode can significantly alleviate the polarization and improve the reversibility of the redox couples in comparison with rGO electrode. The excellent electrocatalytic activity should be attributed to the excellent electrocatalytic performance of RuSe and the good electronic conductivity of rGO. Accordingly, the VRFB cell based on RuSe/rGO modified electrode exhibits enhanced cell performance.

This work was supported by the Key Research Program of the Chinese Academy of Sciences (Grant No. KGZD-EW-202-2), National Natural Science Foundation of China (21271180), the National High Technology Research and Development Program of China (863 Program, No.2013AA050905 and No. 2014AA052303) and the Key Technology Research Projects of Qingdao (No. 12-4-1-24-gx, No.13-4-1-10-gx).

Notes and references

^a Qingdao Key Lab of Solar Energy Utilization and Energy Storage Technology, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, No. 189 Songling Road, 266101 Qingdao, China. Email: cuigl@qibebt.ac.cn

^b The Institute of Physics, Chinese Academy of Sciences, Beijing, 100190 P. R. China.

† These two authors contributed equally to this work.

Electronic Supplementary Information (ESI) available: [Experimental details]. See DOI: 10.1039/c000000x/

- 1 E. Sum and M. Skyllas-Kazacos, *J. Power Sources*, 1985, **15**, 179.
- 2 A. Parasuraman, T. M. Lim, C. Menictas and M. Skyllas-Kazacos, *Electrochim. Acta*, 2013, **101**, 27.
- 3 W. Wang, Q. Luo, B. Li, X. Wei, L. Li and Z. Yang, *Adv. Funct. Mater.*, 2013, **23**, 970.
- 4 C. Flox, J. Rubio-Garcia, R. Nafria, R. Zamani, M. Skoumal, T. Andreu, J. Arbiol, A. Cabot and J. R. Morante, *Carbon*, 2012, **50**, 2372.
- 5 K. J. Kim, M.-S. Park, J.-H. Kim, U. Hwang, N. J. Lee, G. Jeong and Y.-J. Kim, *Chem. Commun.*, 2012, **48**, 5455.
- 6 X. Rui, M. O. Oo, D. H. Sim, S. Raghu, Q. Yan, T. M. Lim and M. Skyllas-Kazacos, *Electrochim. Acta*, 2012, **85**, 175.

- 7 C. Yao, H. Zhang, T. Liu, X. Li and Z. Liu, *J. Power Sources*, 2012, **218**, 455.
- 8 W. G. Zhang, J. Y. Xi, Z. H. Li, H. P. Zhou, L. Liu, Z. H. Wu and X. P. Qiu, *Electrochim. Acta*, 2013, **89**, 429.
- 9 Y. Feng, A. Gago, L. Timperman and N. Alonso-Vante, *Electrochim. Acta*, 2011, **56**, 1009.
- 10 Y. Feng and N. Alonso-Vante, *Phys. Status Solidi B*, 2008, **245**, 1792.
- 11 H.-Y. Park, S. J. Yoo, S. J. Kim, S.-Y. Lee, H.C. Ham, Y.-E. Sung, S.-K. Kim, S. J. Hwang, H.-J. Kim, E. Cho, D. Henkensmeier, S.W. Nam, T.-H. Lim and J. H. Jang, *Electrochim. Commun.*, 2013, **27**, 46.
- 12 P.J. Kulesza, K. Miecznikowski, B. Baranowska, M. Skunik, S. Fiechter, P. Bogdanoff, I. Dorbandt, *Electrochim. Commun.*, 2006, **8**, 904.
- 13 K.-T. Jeng, N.-Y. Hsu and C.-C. Chien, *Int. J. Hydrogen Energy*, 2011, **36**, 3997.
- 14 Z. González, C. Botas, P. Álvarez, S. Roldán, C. Blanco, R. Santamaría, M. Granda and R. Menéndez, *Carbon*, 2012, **50**, 828.
- 15 J. Jin, X. Fu, Q. Liu, Y. Liu, Z. Wei, K. Niu and J. Zhang, *ACS Nano*, 2013, **7**, 4764.
- 16 F. Huang, Q. Zhao, C. Luo, G. Wang, K. Yan, D. Luo. *Chin Sci Bull* 2012, **57**, 4237.
- 17 H.-M. Tsai, S.-J. Yang, C.-C. M. Ma and X. Xie, *Electrochim. Acta*, 2012, **77**, 232.
- 18 P. Han, H. Wang, Z. Liu, X. Chen, W. Ma, J. Yao, Y. Zhu and G. Cui, *Carbon*, 2011, **49**, 693.
- 19 P. Han, Y. Yue, Z. Liu, W. Xu, L. Zhang, H. Xu, S. Dong and G. Cui, *Energy Environ. Sci.*, 2011, **4**, 4710.
- 20 E. Sabatani and I. Rubinstein, *J. Phys. Chem.*, 1987, **91**, 6663.
- 21 C. Saby, B. Ortiz, G. Y. Champagne and D. Bélanger, *Langmuir*, 1997, **13**, 6805.
- 22 L. Yue, W. Li, F. Sun, L. Zhao and L. Xing, *Carbon*, 2010, **48**, 3079.