

## **Electronic Supplementary Information (ESI)**

# **Novel catalytic effects of Mn<sub>3</sub>O<sub>4</sub> for all vanadium redox flow batteries**

Ki Jae Kim, Min-Sik Park, Jae-Hun Kim, Uk Hwang, Nam Jin Lee, Goojin Jeong and  
Young-Jun Kim\*

Advanced Batteries Research Center, Korea Electronics Technology Institute,  
Seongnam, Gyeonggi 463-816, Republic of Korea.

Fax: +82-789-7499; Tel: +82-789-7490; E-mail: [yjkim@keti.re.kr](mailto:yjkim@keti.re.kr)

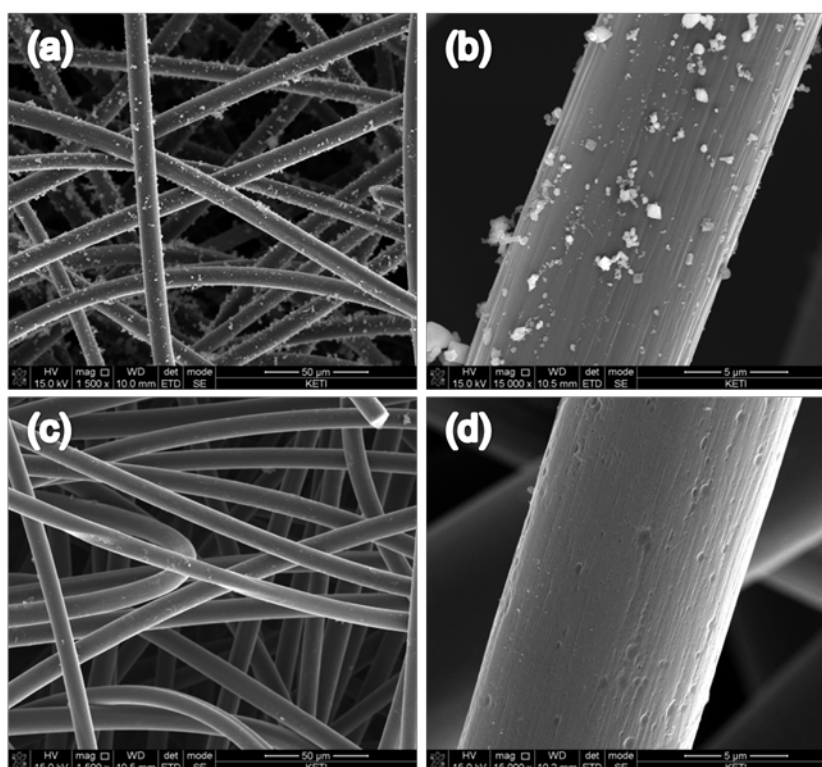


Figure S1. SEM images of carbon felt modified with  $\text{Mn}_3\text{O}_4$  before cycling at (a) low magnification and (b) high magnification and SEM images of carbon felt modified with  $\text{Mn}_3\text{O}_4$  after cycling at (c) magnification and at (d) high magnification, respectively.

As shown in Figure S1 (a) and (b), it is clearly observed that  $\text{Mn}_3\text{O}_4$  nanoparticles on the surface of the carbon felt are well attached before charging and discharging. However, after cycling, those particles are washed away by electrolyte flowing. This result indicates that the adhesion between  $\text{Mn}_3\text{O}_4$  nanoparticles and surface of carbon felts is very weak.

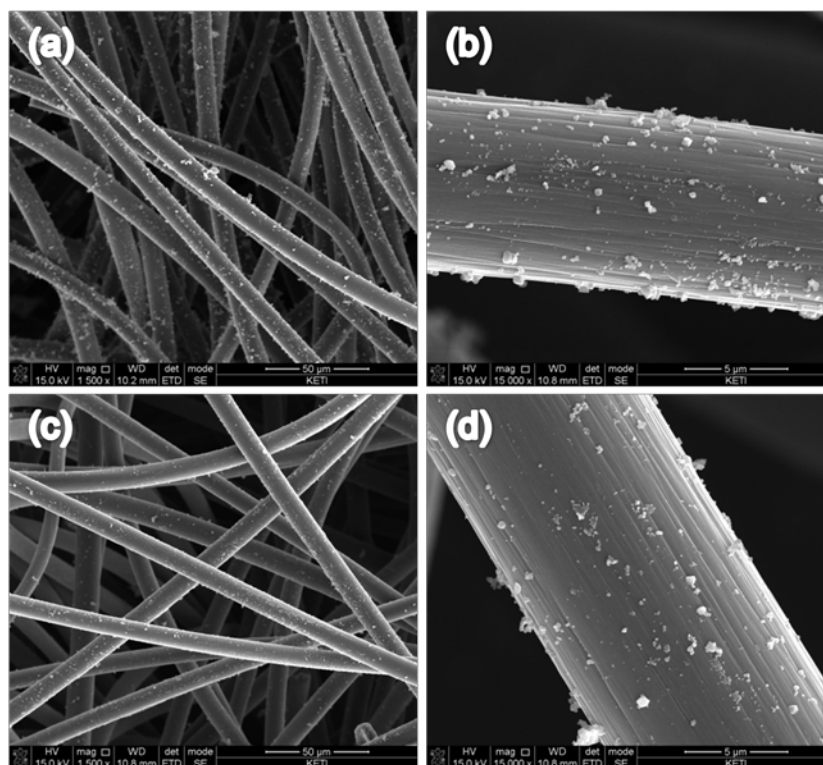


Figure S2. SEM images of carbon felt modified with  $\text{Mn}_3\text{O}_4$  after heat treatment at 500 °C for 5 h under an Ar atmosphere at various magnifications. (a) and (b) before cycling, and (c) and (d) after cycling in the flow cells.

As shown in Figure S2, it is found that  $\text{Mn}_3\text{O}_4$  nanoparticles on the surface of the carbon felt are well attached before and after cycling. This result reveals that the adhesion between  $\text{Mn}_3\text{O}_4$  nanoparticles and surface of carbon felts is dramatically improved by heat treatment under an Ar atmosphere.

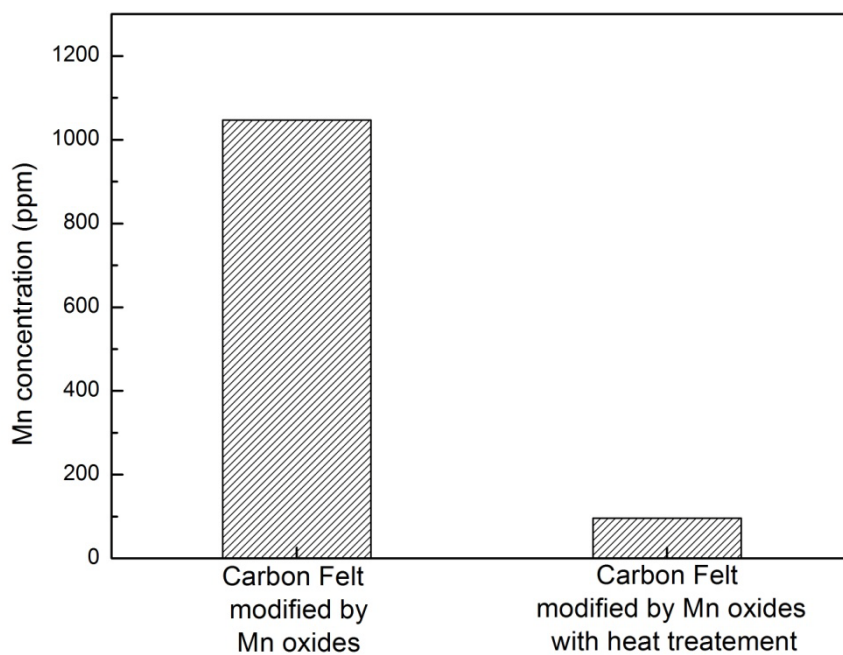


Figure S3. Comparison of Mn concentrations in the electrolytes of the VRFB cells employing carbon felt modified with  $\text{Mn}_3\text{O}_4$  after cycling with and without the heat treatment under an Ar atmosphere.

The Mn concentration was analyzed by the inductively-coupled plasma and atomic absorption spectroscopy.

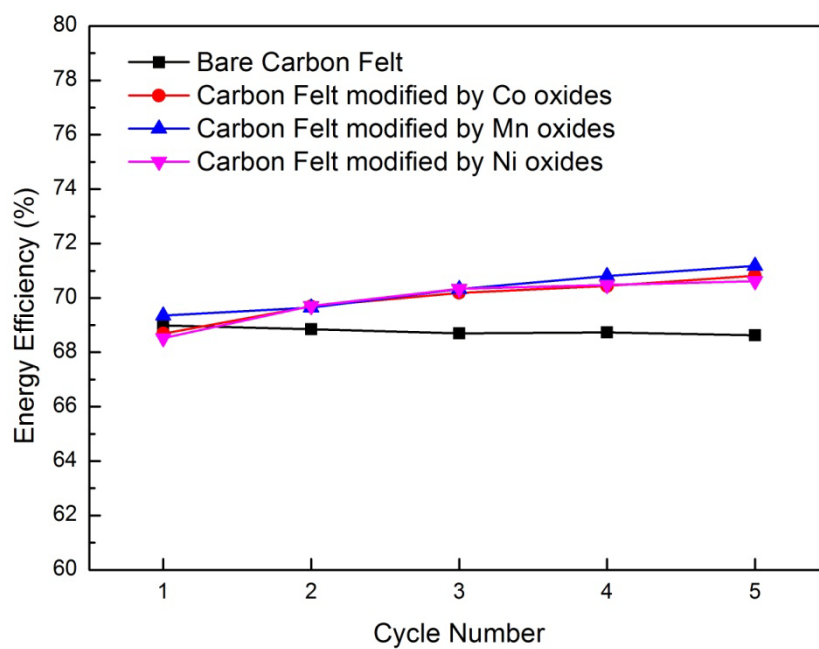


Figure S4. Energy efficiencies of the VRFB cells that employed carbon felt electrodes modified with various metal oxides.

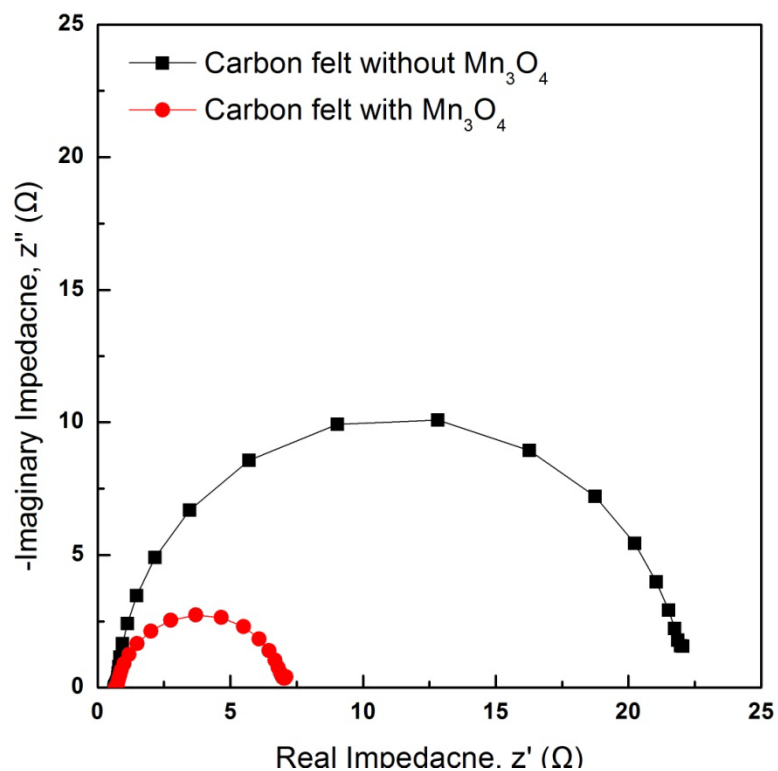


Figure S5. Electrochemical Impedance Spectroscopy (EIS) of the carbon felt with and without  $\text{Mn}_3\text{O}_4$ .

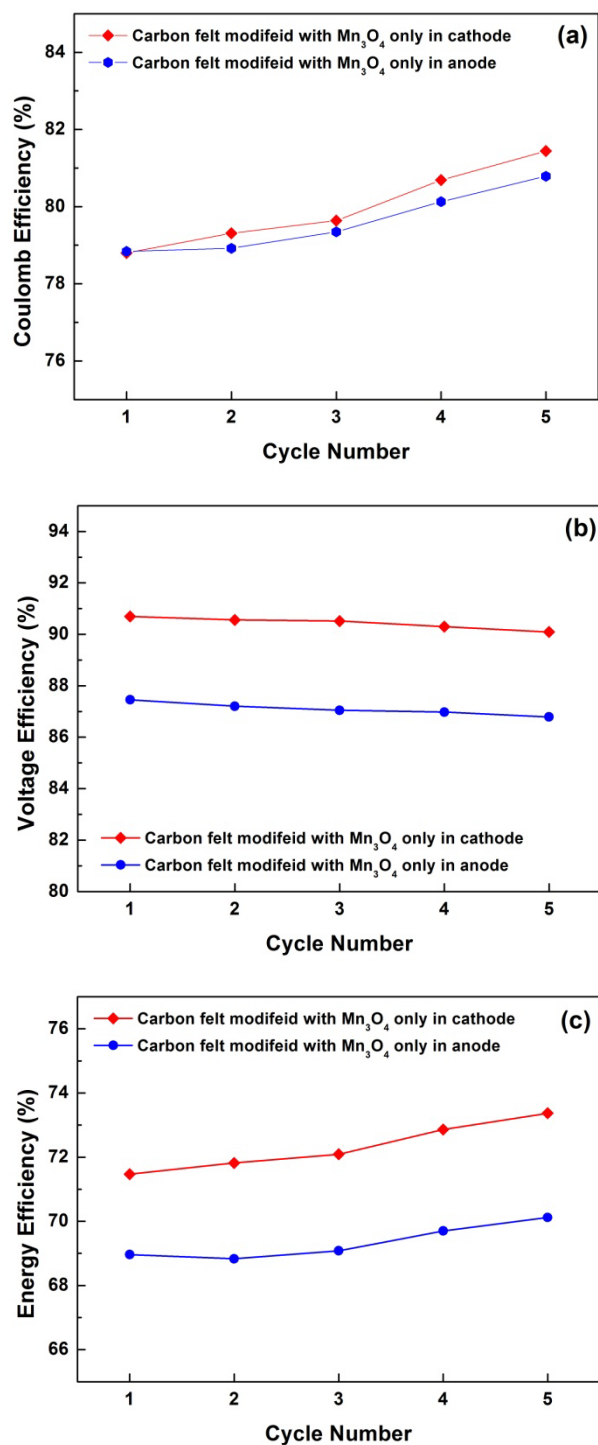


Figure S6. Comparison of electrochemical performance between VRFB cells employing carbon felt modified with  $\text{Mn}_3\text{O}_4$  only in cathode and that only in anode; (a) coulomb efficiency, (b) voltage efficiency and (c) energy efficiency.