The vanadium flow battery (VFB) is probably to be one of the most promising large scale energy storage systems for smoothing the power output of renewable energy electricity like photovoltaic (PV) and wind generated electricity, due to its advantages such as high safety and reliability, environmental friendly, high energy efficiency [1]. Perfluorinated membranes, such as Dupont Nafion® series, are the most commonly used membranes in VFBs due to their excellent stability and proton conductivity [2]. However, they suffer from high cross-mixing rate of vanadium ions [3]. The morphology of ion exchange membrane plays a crucial role in determining membranes properties in VFB, especially their ion selectivities. It has been reported that the length of side chains has strong effect on microstructure of the membranes and finally determines their performance [4].

In this work, perfluorinated membranes with different length of side chains were selected and investigated with respect to their morphology and electrochemical properties in VFB. Small angle X-ray scattering could give quite reliable information on the hydrophobic/hydrophilic segregation in the amorphous part of the ionomer [5]. As shown in Figure 1, an ionomer peak at q-value of about 2.2 nm⁻¹ is appeared in SSC-M2 membranes, which is larger than that of NF115 (q=1.65 nm⁻¹). As a result, the Bragg spacing of SSC-M2 (d=2.854 nm) is much smaller than that of Nafion, indicating lower degree of phase segregation of SSC-M2 membranes. The result of SAXS indicated that membrane with shorter side chains (SSC-M2) displayed a smaller size of ionic cluster, which is favorable to improve the ion selectivity of membrane.

The volume changes of the electrolytes at the end of charge during the long terms process are shown in Figure 2. Apparently, SSC-M2 shows a remarkable lower degree of net water transfer in the consecutive hundreds of cycles compared to LSC-NF115. The rate of volumetric reduction at the end of 400th charge is 24% for SSC-M2 at -ve, which is half of NF115 (50%). In-situ mass transfer revealed that the water transfer of SSC-M2 is significantly limited by shrinking its ionic cluster channel compared to LSC-NF115. Consequently, the employment of SSC-M2 contributes to the balance of volume and mass between catholyte and anolyte, thus keeping steady performance of a VFB single cell and easing periodic electrolyte maintenance.

The results indicate that membranes with short side chains are proved to be one of the ideal options in fabricating steady and high performance VFBs.

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Reference: