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Novel Supercapcitor-Battery Energy Storage System with Hybrid Electrolyte for Stationary Application

Shu-Lei Chou *, Yun-Xiao Wang, Jian-Tie Xu, Jia-Zhao Wang, Hua-Kun Liu, and Shi-Xue Dou
Institute for Superconducting & Electronic Materials (ISEM), Innovation Campus,University of Wollongong, Wollongong, NSW, 2519, Australia.
*corresponding author: Email: shulei@uow.edu.au; T: +61-2-42981405

The essential requirements of energy storage device for storing clean energy are low cost, long cycle life, and safety. The volumetric energy density is not that crucial due to the fact that the stationary energy storage system don’t need to move around very often. Supercapacitors can normally achieved a high cycling performance but with relatively low energy density.[1] For example, supercapacitors based on MnO_2 active materials in aqueous electrolyte can be cycled up to 30,000 cycles with capacity retention higher than 80%, but the energy density is less than 10% of LIBs.[2] On the other hand, lithium metal shows a great advantage as anode materials for lithium battery including high theoretic capacity (~3800 mAh g^{-1}) and highly reversible capacity. This has been known in the late of 1970’s.[3] However, the commercial of lithium metal battery is not successful due to the safety issue aroused during cycling. Room temperature ionic liquids (RTILs) which are flame-resistant, nonvolatile, and electrochemical stable can effectively prevent the formation of lithium dendrites, showing potential as the safe electrolytes in lithium battery systems.[4]

Recently, the super ionic conductor glass ceramic film (LiSICON) was proposed as an ionic conducting electrolyte and/or separator for preventing the penetration of lithium dendrite during cycling.[5] Furthermore, novel lithium hybrid electrolyte systems have been proposed by Zhou’s group[6] and Goodenough's group[7] using Cu and $Ni(OH)_2$ as cathode materials.

Here, we propose a hybrid electrolyte system combining the feature of supercapacitors and lithium batteries using MnO_2 nanoflakes in 1M Li_2SO_4 aqueous electrolyte as cathode materials and lithium in 1 M lithium bis(trifluoromethanesulfonyl)imide ($LiNTf_2$) in *N*-methyl-*N*-propyl pyrrolidinium bis(trifluoromethanesulfonyl)imide ($[C_3mpyr][NTf_2]$) electrolyte as anode separated by a LiSICON solid state electrolyte as schematically shown in Figure 1. This system has several advantages. 1) This system shows long cycle life because the MnO_2 shows excellent cycle life in aqueous supercapacitors as reported previously.[2,6,7] 2) Higher specific energy as the working voltage (3.4 V) is almost 6 times higher than that of aqueous based supercapacitors. 3) Safety could be improved by using ceramic solid state electrolyte which can prevent the penetration of lithium dendrites. 4) The active materials used here is MnO_2 which is also cheap and environmental friendly.

The charge and discharge curves in 3 electrode system were exhibited in Figure 1. The potential variations of both the cathode and anode versus reference electrode (RE) can be monitored. Therefore, the charge and discharge curves shown in Figure 1 are plotted versus RE and counter (Li) electrode, respectively. The charge and discharge curves are typical supercapacitor slop curves. The specific capacitance and capacity are 230 F g^{-1} and 50 mAh g^{-1}, which are similar as the previous report.[6] The average working potential is 3.4 V which is a 6 times higher than that of the aqueous system (0.45 V). The specific energy for cathode materials in the hybrid electrolyte system is 170 Wh kg^{-1}, which is much higher than that of the supercapacitor materials. The current density used here is 50 mA g^{-1} which is equal to 1 C rate.

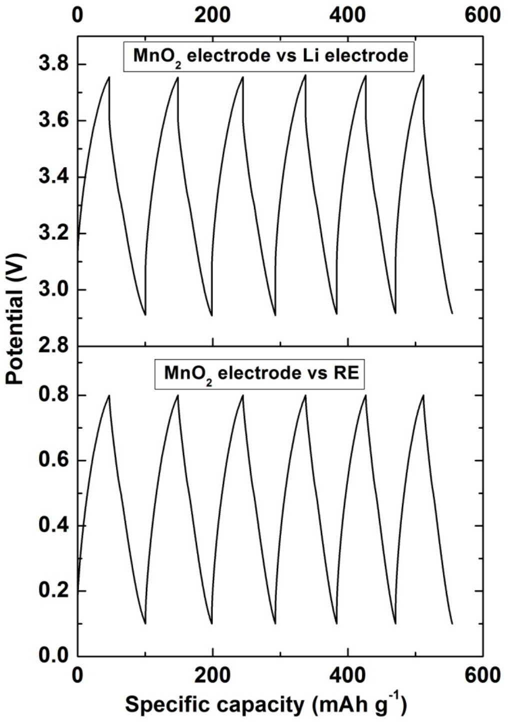

Figure 1. Charge and discharge curves for Li-MnO_2 hybrid electrolyte batteries versus Ag/AgCl reference electrode (bottom) and lithium electrode (top) at a rate of 50 mA g^{-1} using three electrode system between 0.1 and 0.8 V. The specific capacity is calculated based on MnO_2 cathode weight.

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