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Metal-organic frameworks based membrane as a permselective separator for lithium-sulfur batteries

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ABSTRACT

Although lithium-sulfur batteries possess five-fold higher theoretical capacity than the state-of-the-art lithium-ion batteries, the migration of polysulfide between the electrodes remains as a problem area. In order to overcome this issue, numerous strategies have been adopted. Herein, we introduce a novel 1,3,5 benzene tricarboxylate-manganese (Mn-BTC) metal organic framework (MOF) coated-Celgard (2320) separator which acts as permselective in a Li-S cell. The Li-S cell with coated membrane exhibited higher discharge capacity than the uncoated one. The diffusion of polysulfides is successfully blocked by the separator due to the repulsive ionic forces provided by the COO− that is present in the periphery of Mn-BTC MOF which was confirmed by XPS and XRD analyses.

1. Introduction

Over the last three decades several attempts have been made to find alternative energy conversion and storage systems with high power and energy densities in order to meet out the demands from different sectors [1]. Although the state-of-the-art lithium-ion batteries find an unprecedented place in the electronic gadgets such as mobile phones, laptop computers etc., it cannot meet out the demands for the applications in hybrid electric vehicles due to their limitations in the topotactic reactions [2]. Among the systems explored so far, lithium sulfur battery has fascinated the attention of researchers due to its unique advantages such as high theoretical specific capacity (1672 mAh g^{-1}), abundance of sulfur, low cost and better safety [3,4]. In spite of these advantages, the bottlenecks such as low electronic conductivity of sulphur (5×10^{-30} S cm^{-1} at 25 °C), shuttling of polysulfides and poor interfacial properties of lithium metal anode with electrolytes thwart Li-S system from commercialization [5]. Several strategies have been adopted to circumvent these issues such as developing new electrode materials, tuning of the electrolytes by incorporation of various additives, etc.

Although the electronic conductivity of sulfur was considerably improved by encapsulation of sulfur in carbon nanotubes, carbon spheres, graphene and graphene oxides etc., the shuttling of polysulfide between the electrodes still remains a key problem. The solid polymer [6] and glass ceramic electrolytes [7] have also been employed. Unfortunately, the diffusion rate of lithium-ions through the solid electrolytes is very low and thus limits the rate capability of Li-S cells. Ion exchange membranes have also been employed to suppress the shuttle mechanism [8,9]. In a different approach, Nafion layer was coated on a conventional polypropylene membrane to suppress the shuttling of polysulfides between the electrodes [10]. Addition of Nafion resulted in decreased Coulombic efficiency and rate capability (at 2 and 5C rates) and this was ascribed to the poor electronic conductivity offered by Nafion in the electrode. Recent studies have shown that coating of separators with a suitable ion selective material could suppress the polysulfides effectively. In general, ion selective materials/membranes enhance the performance of Li-S batteries in two ways, i) it prevents the loss of sulfur active materials by preventing polysulfide diffusion and ii) it suppresses the shuttle effect caused by the reaction of polysulfide and lithium metal [11]. In a very recent report,

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Ahn and co-workers reported the performance of Li-S cells with montmorillonite (MMT) ceramic protective membrane as an ion selective separator [12]. In a similar way, graphene oxide was also coated on a Celgard 2400 separator in order to block the migration

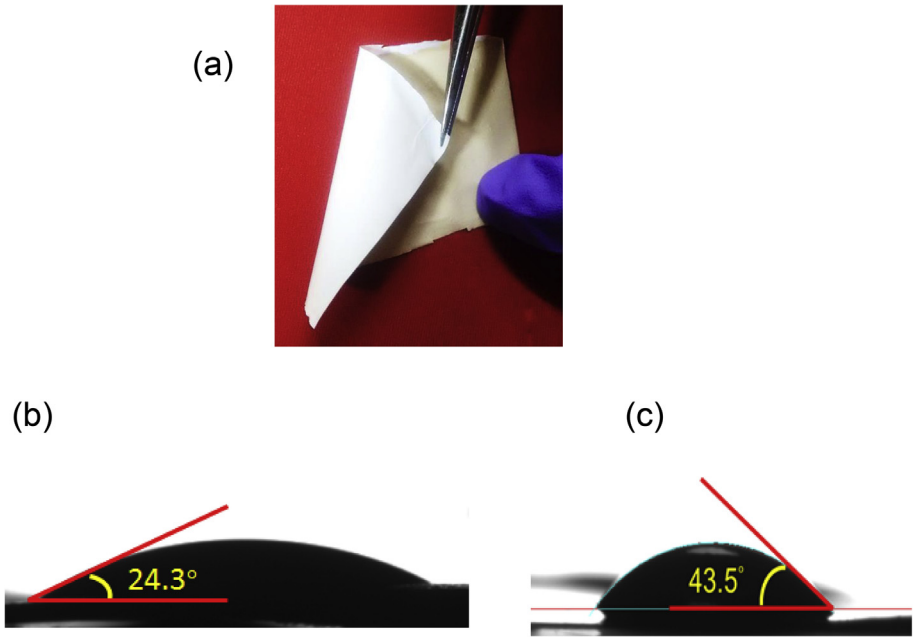

Fig. 1. (a) Digital photograph of the Mn-BTC MOF coated membrane. Contact angle shots of (a) Mn-BTC MOF -coated (b) uncoated membrane.

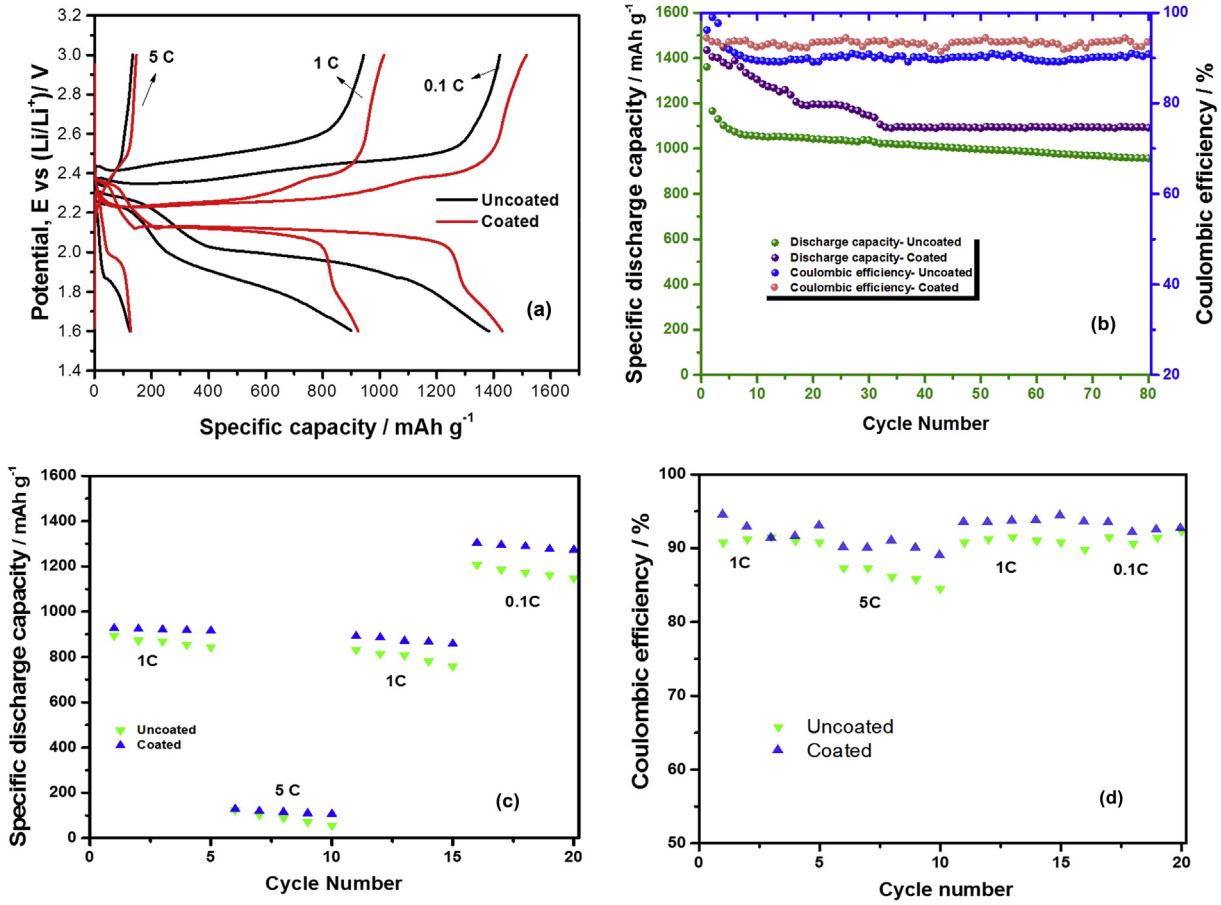

Fig. 2. (a) Cycling profile; (b) Specific capacity and Coulombic efficiency as a function of cycle number for the cell Li-S cell at 0.1 C rate; (c) Specific capacity vs. cycle number at different C-rates and (d) Coulombic efficiency as a function of cycle number for the Li-S cell at different C-rates.