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Enhanced polysulphide redox reaction using a RuO₂ nanoparticle-decorated mesoporous carbon as functional separator coating for advanced lithium–sulphur batteries†

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A multi-functional RuO₂ nanoparticle-embedded mesoporous carbon-coated separator is used as an electrocatalytic and adsorbing polysulphide-net to enhance the redox reaction of migrating polysulphides, to improve active material utilization and boost the electrochemical performance of lithium–sulphur batteries.

Due to the exceptional high theoretical specific energy density of 2.6 kW h kg^{−1}, the lithium–sulphur (Li–S) battery has emerged as a proficient candidate for post lithium-ion battery systems skilled to meet forthcoming energy storage targets set for battery-electric vehicles and smart grids connected with solar or wind power systems.¹ Furthermore, elemental sulphur as the active cathode material is earth-abundant, inexpensive and non-toxic, which is crucial for broad manufacturing applications. However, the mass production of Li–S batteries has been delayed by inherent problems. The insulating nature of sulphur and its reduced species (Li₂S/Li₂S₂), the large volume changes during the lithiation or delithiation process and particularly the so-called shuttle effect are the main reasons of low active material utilization, fast capacity decay, low Coulombic efficiency (CE) and short lifetime of the cells.

To overcome the aforementioned issues, tailored polymer electrolytes and electrolyte additives have been used to prevent the diffusion of soluble lithium polysulphide (LiPS) intermediates to the anode region and inhibit undesirable side reactions on the lithium anode surface.² On the other hand, the incorporation of elemental sulphur into a conductive porous carbon matrix is

an effective strategy to improve the electron conductivity of the cathode and to limit the active material dissolution.³ More recently, the reconfiguration of the Li–S cell by integrating functional carbon interlayers or hybrid separators has demonstrated to be an interesting stratagem to limit the LiPS shuttle, to improve the active material reutilization and indirectly diminish the LiPS passivation of the anode.⁴ However, the poor affinity of carbon hosts and functional carbon-coatings used in, respectively, cathodes and modified separators to interact with polar LiPSs have further prompted the adoption of functionalised carbon materials doped with different heteroatoms (*e.g.* N, S, B, P and their combination).^{5,6} Another promising strategy pioneered by Nazar and co-workers is the employment of hydrophilic and polar metal oxides as host materials (TiO₂,⁷ Ti₄O₇,⁸ MnO₂⁹) to form relatively strong chemical bonds with LiPSs and thus keeping them localised on the cathode side. More recently, conductive metallic nanoparticles (Ni, Pt, Au)^{10,11} have been incorporated to the sulphur cathode to improve the chemical affinity to LiPSs and the overall conductivity. While the aforementioned works have been focused their studies on the cathode material, the introduction of conductive and catalytically active metal oxide nanoparticles (NPs) into functional hybrid separators to enhance LiPS anchoring strength has not yet been reported. RuO₂ is highly conductive (10⁴ S cm^{−1}), chemically very stable and a well-known catalyst for oxidation processes such as chlorine production.¹² Its beneficial properties to the redox reaction of LiPS have not been reported so far.

In this contribution, a functional RuO₂ nanoparticle-decorated mesoporous carbon (RuO₂-MPC)-coated separator is used for the first time as a proof of concept to demonstrate that the employment of catalytic materials with high conductivity in hybrid separators can enhance the LiPS redox reaction and efficiently improve the sulphur (re)utilization, resulting in an advanced Li–S cell with high capacity and remarkable cycling stability. For this purpose, a SiO₂-templated mesoporous carbon (MPC)¹³ was easily functionalised *via* impregnation-hydrothermal oxidation of RuCl₃·*n*H₂O at 200 °C under air (experimental details in ESI†).¹⁴

The morphology of the raw MPC and the obtained RuO₂-MPC were investigated by transmission electron microscopy (TEM).

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Fig. 1 TEM images of (a) pristine MPC and (b) RuO_2 -MPC composite. (c) High-resolution TEM image the RuO_2 -MPC and (d) the corresponding SAED pattern.

Fig. 1a shows the representative structure of the MPC which exhibits a consistently distributed spherical-shaped porous network, proving good structural replication of the corresponding spherical SiO_2 templates. In contrast to the MPC used as support material, the prepared RuO_2 -MPC displays numerous NPs depicted as small grey dots uniformly distributed throughout the carbon matrix (Fig. 1b and Fig. S1, ESI†). The high-resolution TEM image (Fig. 1c) provides further information about the structure of the NPs with an average diameter of ≈ 2 nm. The NPs exhibit crystalline domains evidenced by the distinct lattice planes (white circles) which correspond to the tetragonal rutile structure type of RuO_2 (space group $P4_2/mnm$ ¹⁵) with lattice spacings of ≈ 2.25 Å and ≈ 2.50 Å of the (200) and (101) plane, respectively. The latter finding is further supported by the selected area electron diffraction (SAED) pattern (Fig. 1d) as well as X-ray powder diffraction (XRD) analyses (Fig. S2, ESI†). The corresponding SAED image shows broad ring patterns indicating short range order of the crystalline lattice as a result of the small NPs. The diffraction rings correspond to the (110), (101), (200) and (211) of RuO_2 which is supported by the XRD pattern of the RuO_2 -MPC composite showing broad reflections of RuO_2 . By Rietveld analysis we could determine a crystallite size of 6 nm which matches well with the crystallite sizes obtained by TEM (Fig. S2, ESI†). These results evidence the successful formation of RuO_2 NPs anchored to the carbon wall of the MPC. It is worth mentioning that the final RuO_2 content was determined by thermogravimetric (TGA) analysis and accounts to 25 wt% (Fig. S3, ESI†). The physical features of the MPC and RuO_2 -MPC were investigated by nitrogen physisorption isotherms (Fig. 2 and Table S1, ESI†). The isotherm of the MPC displays the characteristic combination of type I and type IV isotherms, indicating the presence of micropores and mesopores.¹⁶

Note that distinct hysteresis loop at relatively high pressure to fill the pores with N_2 evidences a large pore volume in the

Fig. 2 (a) Nitrogen physisorption isotherms and (b) pore size distributions of the MPC and RuO_2 -MPC.

material. The specific surface area (SSA) determined by the Brunauer–Emmett–Teller (BET) method and the total pore volume are calculated to be $528 \text{ m}^2 \text{ g}^{-1}$ and $1.92 \text{ cm}^3 \text{ g}^{-1}$, respectively. Furthermore, the pore size distribution (PSD) derived from the QSDFT equilibrium model (Fig. 2b) shows micropores and mesopores with diameters of, respectively, 0.7 and 12.5 nm, which is in good agreement with the 12 nm-in-diameter of the spherical, commercial SiO_2 template. In comparison to MPC, RuO_2 -MPC shows both lower SSA ($343 \text{ m}^2 \text{ g}^{-1}$) and lower pore volume ($1.69 \text{ cm}^3 \text{ g}^{-1}$). The decrease in SSA and pore volume is due to RuO_2 NPs addition which increases the relative density of the RuO_2 -MPC composite. However, the obtained RuO_2 -MPC still possesses relatively high surface area and large pore volume to guarantee high sulphur-species loading and to accommodate the volume changes of sulphur during the lithiation/delithiation processes without impeding fast Li^+ -ion diffusion.

The combination of the uniform distribution of conductive RuO_2 NPs and the large electrochemically active surface of the RuO_2 -MPC composite could ensure a strong affinity of LiPSs to the carbon matrix, to further enhance redox reaction kinetics, to improve active material utilization and to finally boost overall cell performance. In order to provide the proof-of-the-concept, a hybrid RuO_2 NP-anchored MPC-coated separator (RuO_2 -MPC-HS) was easily prepared by direct casting of the carbon composite slurry on one side of the commercially used Celgard polypropylene (PP) separator *via* the doctor blade method (fabrication details in ESI†).^{6,16} By this simple approach, a thin RuO_2 -MPC composite-coating of $\approx 16 \mu\text{m}$ is well-adhered onto the PP separator (Fig. 3). The added areal mass loading of the coating is 0.3 mg cm^{-2} , corresponding to only 30 wt% of the pristine separator. To cross-check the improved sulphur retention and utilization properties, a hybrid separator consisting of a carbon black (Super P)-mesoporous carbon-coating (SP-MPC-HS) was used. It is worth mentioning that the used content of SP in the mixture corresponds to the weight content found for the RuO_2 NPs in the carbon composite (Fig. S3, ESI†). In this way, we can ensure fair electrical conductivity and somewhat similar physical properties (Table S1, ESI†) in both functional coatings and thus a possible electrocatalytic effect resulting from the RuO_2 NPs could be easily distinguished from other contributions. It is noteworthy that a pure sulphur cathode (with a sulphur content of 70 wt%) is utilised with this type of hybrid separators instead of sophisticated sulphur-based composite cathodes.^{16,17} As shown in

Fig. 3 (a) Photographic image of the pristine separator and the prepared RuO₂-MPC-HS. (b) Cross-sectional SEM image and the corresponding EDX elemental mapping of the RuO₂-MPC-HS.

Fig. S4 (ESI[†]), the electrochemical impedance spectroscopy (EIS) plots of the fresh cells with pristine and hybrid separators show a high decrease of the charge transfer resistance (R_{CT}) by over 72% after substituting the PP separator by the hybrid separators. Furthermore, the R_{CT} value of the cell with a RuO₂-MPC-HS (34 Ω) is lower than that for the cell with a SP-MPC-HS (39 Ω), indicating that the RuO₂-MPC-coating offers additional electron pathway to the resistive sulphur cathode.^{16,18} Fig. 4a shows the representative cyclic voltammetry (CV) curves of the Li-S cells with RuO₂-MPC-HS and SP-MPC-HS at a scan rate of 0.05 mV s⁻¹. Both cells present two separated cathodic peaks at ≈ 2.32 V and ≈ 2.04 V ascribed to (I) the conversion of elemental sulphur to soluble higher-order LiPSs and (II) their further reduction/precipitation to Li₂S₂/Li₂S, respectively. On forward process, two anodic peaks attributed to (III) the formation of higher-order LiPSs and (IV) the final conversion to elemental sulphur are observed. While the cell with a SP-MPC-HS displays somewhat overlapped anodic peaks (III and IV), the oxidation peaks III and IV are better separated for the RuO₂-MPC-HS. The cell with a RuO₂-MPC-HS shows a positive shift in the reduction peaks (I and II) and evident negative shifts in the oxidations peaks (III and IV) compared with the SP-MPC-HS, but also presents narrower full width at half-maximums (FWHM) and higher current densities (Table S2, ESI[†]), in particular for the two oxidation peaks III and IV.

Similar observations are made for Pt-containing graphene electrodes in combination with Li-S batteries.¹⁸ In addition, the electrochemical results (Table S2, ESI[†]) demonstrate the superior catalytic activity of RuO₂ to the redox reaction of sulphur-related species.^{10,19} The galvanostatic discharge/charge voltage profiles

Fig. 4 Comparative (a) CV curves, (b) galvanostatic discharge/charge voltage profiles and (c) combined cycling performance of the Li-S cells with SP-MPC-HS and RuO₂-MPC-HS.

recorded at a current rate of 0.1C (Fig. 4b) exhibit a higher discharge capacity and lower cell polarization (ΔE) for the cell with a RuO₂-MPC-HS (1175 mA h g⁻¹ and 136 mV, respectively) compared with the SP-MPC-HS (1081 mA h g⁻¹ and 150 mV, respectively). These higher active material utilization and lower polarization for the cell with a RuO₂-MPC-coating, as well as the position of the voltage plateaus I, II, III and IV (Fig. 4b) are in good agreement with the CV profiles shown in Fig. 4a. The cycling stability of the Li-S cells with both hybrid separators was studied by performing a combined cycling test conducted at different current rates (0.1, 0.2 and 0.5C) as shown in Fig. 4c. The cell with a RuO₂-MPC-HS delivers an initial discharge capacity of 1276 mA h g⁻¹ at 0.1C. After 10 cycles, the cell stabilizes its capacity reaching a value of 1066 mA h g⁻¹ (Fig. S5a, ESI[†]). In the case of the SP-MPC-HS, both the initial discharge capacity and the capacity after stabilization (cycle 10) are lower than that found for RuO₂-MPC-HS (1147 and 1009 mA h g⁻¹, respectively). Furthermore, the RuO₂-MPC-HS based cell operated at 0.2 and 0.5C displays, respectively, highly reversible capacities of 859 mA h g⁻¹ (cycle 100) and 665 mA h g⁻¹ (cycle 300), corresponding to an overall remarkable degradation rate of only 0.052% per cycle and a CE of 98.3% (after cell stabilization, 10 cycles). In contrast, the cell with a SP-MPC-HS shows inferior electrochemical performance in terms of capacity retention and cycling reversibility (Fig. S5 and Table S3, ESI[†]), further highlighting the positive effect of the RuO₂ NPs to electrocatalytically enhance the redox reaction of the active sulphur-based material and thus improve the overall electrochemical performance of the Li-S cells.^{10,11} However, both reconfigured cell systems work very well in comparison with sophisticated sulphur-infiltrated porous carbon composite cathodes,^{16,20} which highlights how simple and powerful is this kind of hybrid separator-comprising cell configuration for practical applications. It is worth mentioning that cycling performance tests using hybrid separators modified with a layer of

SP/PVDF (SP-HS) and commercial RuO₂ NPs/PVDF (cRuO₂-HS) also demonstrated that Li-S cells with a cRuO₂-HS delivered a higher specific capacity and higher CE than that cells with SP-HS (Fig. S6, ESI†). Further galvanostatic discharge/charge voltage profiles and cyclic stability of the cells built with RuO₂-MPC as cathode reveal a negligible capacity contribution of $\approx 25 \text{ mA h g}^{-1}$ to the overall capacity (Fig. S7, ESI†), demonstrating that the RuO₂-MPC composite itself is not electrochemically active in the applied potential window (1.8–2.6 V).

To study any possible LiPS adsorption effect from the RuO₂ NPs, LiPS adsorption experiments were performed (further experimental details in ESI†). Relative LiPS adsorptivity studies revealed that the RuO₂-MPC composite is capable to adsorb about 16% more LiPS than a SP-MPC mixture (Fig. S8, ESI†). This higher LiPS affinity of the RuO₂-MPC composite also enhances the hybrid separator abilities to capture and reactivate migrating LiPS species and thus improve the active material reutilization.

In summary, RuO₂ NPs were used for the first time in a Li-S battery system to boost its electrochemical performance. As a proof-of-concept, a multifunctional RuO₂ NP-anchored MPC hybrid separator was used as a polysulphide barrier which not only facilitates electron transport but also enhances the redox reaction of migrating polysulphides by their early adsorption and trapping in the composite-coating and thus retaining the active material in the cathode side to further improve its reutilization. As main result, the pure sulphur cathode with the RuO₂-MPC hybrid separator delivered a high initial discharge capacity (1276 mA h g^{-1} at 0.1C) and demonstrated a long-term cycling stability (over 300 cycles) with high CE (98.2%) and astonishing capacity retention (decay rate of 0.022% per cycle, over 200 cycles at 0.5C). Despite we focused the catalytic effect of the RuO₂ NPs based on the electrochemical results, further work is needed to fully understand the catalytic behaviour of the RuO₂ on the improved sulphur-based redox reaction kinetics. We believe that the implementation of RuO₂ NPs in the design of hybrid separator as well also as one of the component in sulphur cathode promises a new perspective for further improvements in advanced Li-S battery systems.

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