Lithium-ion batteries (LIBs) are very important power sources since 1991. They can be used in many portable small electronic devices and electric vehicles due to the high capacity, long cycling and high energy density [1, 2]. New cathode materials need to be developed and improved for high energy applications as electric vehicles. Sulfur is considered to be one of the most promising cathode materials for next-generation LIBs due to the high theoretical capacity (1672 mAh/g) [3], abundant reserves and nontoxic nature. However, a few drawbacks are related to Li-S batteries such as low conductivity, polysulfide shuttle mechanism or short life time. The theoretical capacity of sulfur coupled with the average operating voltage of a Li-S cell (2.15 V versus Li+/Li0) and the theoretical capacity of a pure lithium anode (3862 mAh/g) gives the energy density as high as ~2500 Wh/kg. Although Li-S batteries possess many advantages, low active material utilization, capacity degradation, self-discharge, poor Coulombic efficiency, poor cycle life, and electrode volume expansion are still the challenges remaining with the Li-S cells [4].

Electroactive conducting polymers (ECPs) are conjugated polymers that exhibit electronic conduction when partially oxidized or reduced and are capable of undergoing oxidation/reduction reactions [5, 6]. Examples of ECPs include polypyrrole (PPy), polyaniline, polythiophene and polyphenylene vinylene. Several of these polymers have been tested as cathode materials for lithium batteries. Polypyrrole, for instance, can act as a host material for Li+-ion insertion/extraction in the voltage range of 2.0-4.5 V versus Li/Li0, with a theoretical capacity of 72 mAh/g [7]. Therefore, PPy is a possible additive which can be used both as a conductive agent as well as a polymeric cathode material.

Herein, we report a simple preparation technique of sulfur-PPy/PEG composites with improved conductivity and stability.

Keywords: lithium, sulfur, batteries, polypyrrole, conductivity
used for all measurements consisted of 0.25 M LiNO₃ and 0.7 M LiTFSI dissolved in DME-DIOX (2:1).

2.3 Sample characterization

Galvanostatic charge/discharge measurements were performed within a potential window from 1.0 to 3.0 V₉₉Li, at different C-rates. CV curves were recorded in the potential window from 1.0 to 3.0 V₉₉Li and the scan rate was set to 0.1 mV/s. All electrochemical measurements were performed with Autolab potentiostat at room temperature. A typical sulfur mass loading on the electrode was 0.8-0.9 mg/cm². Scanning electron microscope JEOL JSM-7000F + EDX INCA were used to observe the structure, morphology and composition of samples.

3. Results and discussion

Figure 1 shows the SEM image of S-C-PPy13% composite cathode materials. We can see the porous agglomerated particles after polymerization of PPy, EDX elemental mapping confirmed homogeneous distribution of carbon, PPY and sulfur. Carbon and polymer composite created a continuous coating and sulfur
The electrochemical impedance spectra (EIS) of different S-C-PPy samples at open circuit potential are shown in Figure 3 a, b. The charge-transfer resistance (Rct) of the S-C sample with 13 wt. % of PPy and 0.5 wt. % of PEG additive (75 Ω) is much smaller than that of the S-C-PPy sample without PEG additive (330 Ω). This result supports the hypothesis that the insulating polymer PEG improves electron and ion transport in the cathode and charge-transfer resistance of Li⁺ ion is improved due to improved mechanical properties of PPy-PEG composite.

Galvanostatic charge/discharge measurements are shown in Figure 4 a, b. The S-C sample with 13 wt. % of PPy and 0.5 wt. % of PEG shows the faster electrochemical reaction with a smallest polarization compared with other samples. This result is in agreement with our previous EIS measurements. The highest discharge capacity observed for sample with PEG additive was 1325 mAh/g-sulfur at a current density of 0.1 C. The discharge was accommodated in pores of carbon and polypyrrole. Smooth conductive layer can enhance the electron transfer and improve the total efficiency of Li-S battery.

Figure 2 shows the cyclic voltammograms (CV) of the composite electrode (S-C sample with 13 wt. % of PPy and 0.5 wt. % of PEG) for the 1st and 2nd cycle. During the first reduction process (discharging), two typical peaks at 2.38 and 2.1 V are observed, corresponding to the reduction of elemental sulfur and to long-chain polysulfide (Li₁S₈, n ≥ 8) and further to short-chain polysulfide (such as Li₂S₆, Li₂S₄) [8, 9]. In the subsequent anodic scan (charging), an intense, broader characteristic peak was observed at 2.5-2.6 V, reporting oxidation of sulfides to elemental sulfur. Anodic and cathodic current for the second cycle was decreased due to the partially irreversible reaction and formation of insoluble polysulfides.

The electrochemical impedance spectra (EIS) of different S-C-PPy samples at open circuit potential are shown in Figure 3 a, b. The charge-transfer resistance (Rct) of the S-C sample with 13 wt. % of PPy and 0.5 wt. % of PEG additive (75 Ω) is much smaller than that of the S-C-PPy sample without PEG additive (330 Ω). This result supports the hypothesis that the insulating polymer PEG improves electron and ion transport in the cathode and charge-transfer resistance of Li⁺ ion is improved due to improved mechanical properties of PPy-PEG composite.

Galvanostatic charge/discharge measurements are shown in Figure 4 a, b. The S-C sample with 13 wt. % of PPy and 0.5 wt. % of PEG shows the faster electrochemical reaction with a smallest polarization compared with other samples. This result is in agreement with our previous EIS measurements. The highest discharge capacity observed for sample with PEG additive was 1325 mAh/g-sulfur at a current density of 0.1 C. The discharge
monomere in acid solution and by evaporation of sulfur into the pores of carbon-polyppyrole composite matrix. To explore the effect of PPy-PEG additive, a series of samples with various content of PPy were investigated to optimize the electrode conductivity, porosity and performance. With increasing amount of PPy porosity was increasing but conductivity was decreasing. After optimization of composition between the sulfur, PPy and PEG a series of electrochemical measurements was performed. As the result, S-C sample with 13 wt. % of PPy and 0.5 wt. % of PEG delivers an optimal discharge capacity of 1300 mAh/g-sulfur at 0.1C after 45 cycles, which owns to improved balance between two components. This material will indicate a new route to rationally design cathode materials for Li-S batteries with superior stability and performance.

Acknowledgement
This research was sponsored by the NATO Science for Peace and Security Programme under grant 985148 and by the project VEGA 1/0074/17.

References