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Development of sulfur based polymers for rechargeable lithium batteries.

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Lithium-ion (Li-ion) batteries are in the front edge of recent achievements concerning energy storage. However, Li-ion devices are reaching their maximum regarding energy density storage which restricts their application in systems with large power needs, such as electric vehicles. Driven by this shortcoming, in the last few years, Lithium-Sulfur (Li-S) batteries are being considered as an alternative for the exploitation of energy storage and conversion systems with improved performance. Indeed, to the S cathodes is associated a theoretical specific capacity of 1672 mA h g^{-1} and a specific energy of 2600 W h kg^{-1}, which are several times higher than the correspondent to other possible systems. The relative low atomic weight of S in comparison with other elements (e.g. cobalt) and the multi-electron transfer reactions in the pair Li/S are at the source of this superior theoretical performance of Li-S batteries. Nonetheless, different kinds of issues such as the polysulfides formation (causing the shuttle effect in the electrolyte), the poor conductivity of sulfur and the increase of specific volume observed during discharge, lead to a poor stability of the S cathodes with concomitant battery performance degradation after some discharge-charge cycles. Different strategies are being considered in the scientific community to counteract these effects, namely the use of S composite materials, the change of electrolytes to control the shuttle effect or the S encapsulation to avoid the expansion phenomena.[1] Furthermore, a new approach based on the inverse-vulcanization of elemental sulfur was recently proposed to improve the stability of S-based cathodes.[2] Through a ring-opening polymerization, the elemental S is transformed into a polymer network and it was demonstrated that these sulfur-rich copolymers can be used in cathodes of Li-S batteries with enhanced charge capacity and lifetime (e.g 1000 mA h g^{-1} capacity and 500 charge-discharge cycles).[2]
Very recently, it was shown by our research group that the inverse-vulcanization of S can be carried out with a high degree of control using Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerization and that many new synthesis pathways can be implemented with possible impact in the improvement of the S based cathodes.[3] Here, we present new findings concerning the synthesis, characterization and application of sulfur based polymers in rechargeable Li batteries. Using cyclic voltammetry (CV), it is shown that the synthesized S-networks preserve the fundamental electrochemical activity of the elemental S. Using split test cell type devices, Li-S batteries were assembled with the produced S-networks in the cathodes and submitted to charge-discharge cycling studies (see Figures 1 and 2 below presented). Results thus obtained evidence that the developed S-networks are promising materials to enhance the performance of Li-S batteries concerning their capacity and cycling stability.

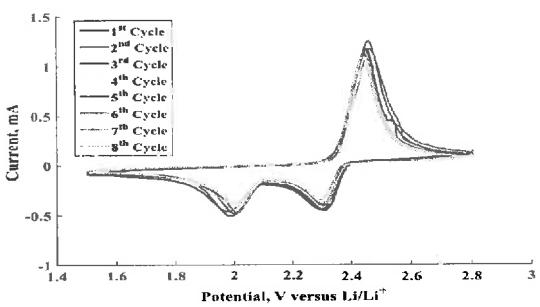

Figure 1: Cyclic voltammograms of a Li-S electrochemical cell assembled with a RAFT synthetized sulfur-polymer as active material in the cathode. Testing performed at the scan rate of 20 μV s^{-1}.

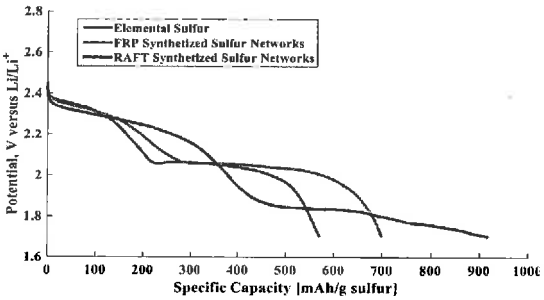

Figure 2: Initial discharge voltage profiles of Li-S cells assembled with cathodes composed of elemental sulfur, FRP and RAFT sulfur-polymers. Testing performed at the C/4 rate.

References:

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[3] C Almeida, H Costa, P Kadhirvel, AM Queiroz, RCS Dias, MRPFN Costa, Journal of Applied Polymer Science, 2016, In Press (DOI: 10.1002/APP. 43993).