DEVELOPMENT AND CHARACTERIZATION OF MnO$_2$ ELECTRODES FOR LITHIUM-AIR BATTERIES

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ABSTRACT – The development of new energy storage technologies is the next step toward sustainability, mainly for the automotive environment, which contributes highly to green-house-gases emissions. In the present work, an air-cathode for the lithium-oxygen batteries was developed by electrodeposition of manganese oxide on a stainless-steel net, and then cycled at different current densities. The capacity obtained was lower than that of lithium-ion batteries, but the research revealed paths for improvements for future works.

1. INTRODUCTION

In 2010, transportation was responsible for 16% of total CO$_2$ emissions, which is the main responsible for greenhouse effect (Ritchie and Roser, 2018). In order to fight climate changes without harming global development, emerged the need to substitute internal combustion engine vehicles (ICEVs), whom run on fossil fuels, by hybrid or electric vehicles (EVs). These, combined with a renewable source of primary energy, are the key to achieving sustainability in transportation (Wagner et al., 2010). The International Energy Agency (IEA) estimates a fleet of almost 300 million electric cars in 2040 (IEA, 2017). However, state-of-the-art lithium-ion batteries have an energy storage limitation, which makes it harder to provide the autonomy required for EVs to replace ICEVs.

Lithium-oxygen (Li-O$_2$) batteries appear as a future promise in the energy storage field. With a theoretical specific energy ten times higher than that of lithium-ion technology, the reaction between metallic lithium and atmospheric or pure oxygen gas has been drawing increased attention in the last few years (Bruce et al., 2012). Though promising, Li-O$_2$ has several challenges to overcome before turning into a practical prototype, such as its poor-rate capability, low round-trip efficiency and short cycle life (Jung et al., 2016). The air cathode has been identified as the dominating factor regarding the battery performance (He et al., 2017). Thus, the development of a good gas-diffusion electrode incorporating a low-cost catalyst for the oxygen evolution and reduction reaction is the main step into improvement (Bruce et al., 2012).

The objective of this study was to develop an electrode for lithium-oxygen batteries by electrodeposition of manganese oxide on a stainless-steel net. Manganese oxide is a promising active electrode material due to its high specific capacitance, low cost, abundance and environmental friendliness (Wei et al., 2011). The electrodeposition technique was chosen because it has easy-to-control parameters and is a one-step process. Furthermore, the electrode
was characterized in order to determine improvement paths for future research.

2. METHODS

The chosen material for the air cathode was a stainless-steel net, 400 mesh, due to its porosity and low cost. It was cut out as a two-dimensional “lollipop” with a three-sheets thickness and cleansed with NaOH 10% and H₂SO₄ 1% for 2 and 1 minutes, respectively. Afterwards, it was kiln-dried for 25 minutes, with a pause in the middle to apply a protection outside the electrodeposition area.

Electrodeposition was conducted on VersaSTAT 3 potentiostat, by Princeton Applied Research. Bath conditions were 0.1 M for both Na₂SO₄ and Mn(CH₃COO)₂ and rotation set on 100 rpm. The parameters set were based on Oliveira et al. (2017). The technique uses a loop of cyclic voltammetry and potentiostatic for 3 times. The cyclic voltammetry was conducted between 0.345 V and 0.645 V, with a Sweep Speed of 0.5 V/s, during 30 seconds. The potentiostatic was set at 0.645 V for 90 seconds. Then, the electrode was washed with distilled water, dried, weighed and stored in the Glove Box (Labstar Mbraun). The catalyst mass deposited on the surface of the electrode was determined by the difference between the mass before and after electrodeposition.

The battery was assembled inside the Glove Box, with low concentrations of H₂O and O₂ (under 1 ppm) and it was composed of: the anode, a disk of metallic lithium (1 cm of diameter); 100 μL of electrolyte solution, being DMSO + lithium perchlorate 0,1 M; the cathode; and a steel net and a spring, to conduct the electrical current. After assembling, the battery rests for 4 hours before cycling. The cycling was conducted on the same potentiostat described above with the following parameters: 20 cycles, high and low potential off-limit of 3.8 V and 2.2 V respectively and two different currents: 20 μA and 50 μA.

3. RESULTS AND DISCUSSION

The electrodes before and after the cleansing process and after the electrodeposition were characterized by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The results are shown in Figure 1. Analyzing Figure 1A it’s possible to identify three levels of the net. The first one, in highlight, presents unidentified impurities. Figure 1B has significantly less particulate than Figure 1A, which can be attributed to the cleansing process. In Figure 1C, after electrodeposition, a thin cracked layer coats the surface steel nets. Parts of the net who were less accessible don’t present this layer. The analysis of the EDS, Figure 1D, shows the thin layer has a strong manganese signature and confirms it wasn’t able to deposit deep inside the net. The EDS-determined element percentage on the sample corroborates the manganese electrodeposition, (from 1% to 36%).

The as-prepared electrodes were cycled in the lithium-oxygen batteries and the results are displayed on Figure 2. As expected and seen in the literature (Bruce et al., 2012), the performance of the air cathode lowers significantly with the current increase when cycling. In Figure 2A that is confirmed, with the performance at 20 μA almost 5 times higher than that at 50 μA. The capacity is lower than that of state-of-the-art lithium-ion batteries, which stands at 180 mAh/g (Imanishi et al., 2014). It is noticeable the distance between expected potential for charge and discharge and the actual potential observed. For a non-aqueous Li-O₂ battery, the reaction potential is around 3.0 V (Bruce et al., 2011), but the as-prepared battery with the manganese oxide as catalyst showed a discharge potential of 2.7 V and a charge potential higher than 3.8 V (since the off-set for charge was set at 3.8 V, it wasn’t able to show the potential for charge). This indicates the
potential window wasn’t able to fully reverse the products from discharge. This is also perceivable in Figure 2B in the extremely low cyclability of the battery (98% decrease).

Figure 1 – SEM images for the air cathode. Stainless-steel sheets: (A) before cleansing; (B) after cleansing; (C) after electrodeposition. (D) EDS after electrodeposition: red dots represent manganese and green dots represent iron.

Figure 2 – Results obtained after cycling: (A) Comparison between the performance of the
electrode at two different currents and (B) capacity at each cycle for the electrode cycled at 20 μA.

4. CONCLUSION

The performance of the Li-O₂ battery with the air cathode developed above was lower than that of state-of-the-art lithium-ion batteries in both currents. The system still has a lot of obstacles to overcome and this study provided a few paths for future researches in the catalyst area. The lack of deposits inside the stainless-steel nets motivates the reduction on the thickness of the electrode from 3 to 1 sheet, as an increase in the rotation during the electrodeposition. The high overpotential during charge and discharge, which may be attributed to the formation of irreversible by-products, may be contoured combining manganese oxide with another low-cost catalyst, maintaining the development of a low cost and functional air cathode for the lithium-oxygen batteries which is the main goal for the research. Furthermore, varying the parameters of electrodeposition may provide a resourceful way of achieving a crystalline structure of the manganese oxide with better electrochemical properties, combined with an analytical technique to identify such structure.

5. REFERENCES

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