論文の要旨

題目　Investigation of MgH_2 composite electrodes for all-solid-state Li-ion batteries working at room temperature
（室温で動作する全固体リチウムイオン電池用 MgH_2 複合電極の研究）

氏 名　Cano-Banda Fernando

Energy storage plays a vital role in the development of many applications from portable electronics to transportation furthermore generation of electricity. Portable electronics such as smartphones and personal computers are part of our daily life. In our modern world, this kind of devices has become important tools for many activities. From the alarm that waking us up in the morning, managing our agenda, our communications, working instruments and entertainment are in our smartphones, tablets and laptops. The development of these technologies has been strongly supported by the growth of batteries technology. After the commercialization of the first rechargeable Li-ion battery in 1992 by Japanese compony Sony, the market of portable electronics has grown year after year. In fact, in year 1993, they sold 3 million units. Supporting the introduction and development of modern innovative devices for health applications, digital cameras, drones, etc. On the same road, the progress of electric vehicles also depends on energy storage systems capable to offer autonomy compared to gasoline. On the other side, power generation using intermittent energy sources (solar energy, wind energy, etc.) requires high-capacity storage systems to take full advantage of these kinds of energy sources. For example, solar energy can provide a huge amount of energy during the daylight period, some part of this energy could be store and then use during the night when the energy source is not available. In this way, solar energy could be a reliable energy source.

From past to present, various class of batteries including Nickel cadmium batteries, lead acid batteries, lead metal batteries have been focused. Among them Li ion batteries are considered best among the rest due to their higher cycle life, higher energy density, better cyclability, and cost effective. However, achieving all these characteristics is not a simple task, it requires an exhaustive investigation of many aspects, electrode materials, electrolyte materials, optimization of fabrication processes, etc. In this scenery, metal hydrides appear as potential candidates for electrode materials possessing remarkable theoretical capacities. MgH_2 owns a high specific capacity (2036 mAh g^{-1}) which is higher than the commercially available graphite-based electrodes and suitable reaction potential as anode material. All-solid-state batteries have been considered as a possible next-generation battery because it solves some safety issues

associated with liquid electrolytes. The liquid combustible electrolyte of Li-ion batteries is replaced by a solid electrolyte. Also, the use of solid electrolytes can avoid problems such as dendrite formations, which is one of the main concerns about the use of Li-metal electrodes.

In this study several solid electrolytes with suitable properties were selected to study their compatibility with MgH_2, focusing on room temperature operation. Metal hydrides electrodes have been reported operating with solid electrolytes mainly at high temperatures because of limitations of conductivity of solid electrolytes at room temperatures. An earlier study about MgH_2-$LiBH_4$ (electrode-electrolyte) was reported by our research group with remarkable results operating at 120 °C. The high-temperature phase of $LiBH_4$ shows a good conductivity ($>10^{-3}$ S cm^{-1}), However, this phase change from a hexagonal to the orthorhombic structure below 117 °C. The low-temperature phase of $LiBH_4$ has a lower conductivity ($<10^{-5}$ S cm^{-1}) than its high-temperature phase. This drastic difference in conductivity forbids the operation of the battery at room temperatures.

Here, all-solid-state Li-metal batteries were fabricated using different electrolytes, electrolytes with high conductivity at room temperatures. The electrolytes were prepared based on $LiBH_4$ mixed electrolytes: $75LiBH_4+25LiI$, $90LiBH_4+10P_2S_5$, $33LiBH_4+67(80Li_2S+20P_2S_5)$ and $80Li_2S+20P_2S_5$. The batteries were analyzed using electrochemical and XRD characterization techniques.

First section of the study was focused on the halide-stabilized $LiBH_4$. Operation of batteries using $LiBH_4$ at room temperature is strongly limited by the low ionic conductivity of $LiBH_4$. LiI, LiBr and other halides can be used to improve the conductivity of $LiBH_4$ at room temperatures. The electrolyte $75LiBH_4+25LiI$ keeps a high ionic conductivity at room temperature. This improvement in conductivity allows the operation of the MgH_2 electrode at room temperatures. Half-cell batteries shown a good performance during initial cycle (discharge: 1300 mAh/g, reversibility: ~800 mAh/g), but some stability issues produce a low cyclability. An alternative configuration using an $80Li_2S+20P_2S_5$ layer enhance the performance of composite electrode $MgH_2/75LiBH_4+25LiI$/carbon.

Second section was focused on the electrolyte $Li_6PS_5(BH_4)$. This electrolyte was prepared by two methods: $90LiBH_4+10P_2S_5$ and $33LiBH_4+67(80Li_2S+20P_2S_5)$. In both cases, the obtained ionic conductivity was similar and higher than $LiBH_4$ and $80Li_2S+20P_2S_5$ (LPS). The electrodes prepared with this electrolyte can operate at room temperature with a limited capacity. The composite electrode with $90LiBH_4+10P_2S_5$ shown a remarkable capacity and more important with a good stability during cycling. After a comparison keeping the same electrolyte layer (LPS), it was concluded that $90LiBH_4+10P_2S_5$ worked better as ionic conductor in composite electrode. The $90LiBH_4+10P_2S_5$ electrolyte enhanced the reversibility of the conversion reaction. This improvement was attributed to the higher content of $LiBH_4$. Previous reports have shown an effect of hydrogen exchange between $LiBH_4$ and MgH_2, this could be the reason for the improvement of the reversibility of the reaction. For the conversion reaction of MgH_2, the mobility of hydrogen is as necessary as the mobility of Li-ions.

Among all the combinations, the preparation of MgH_2 composite electrode using only $LiBH_4$ was identified as the best option for the preparation of the electrode. However, as was mentioned before battery using only $LiBH_4$ as an electrolyte are not able to operate at room temperature. The use of MgH_2-$LiBH_4$ composite electrode was achievable with the use of an electrolyte layer in the cell. This electrolyte layer consisted of a layer of mixed electrolytes. Among them, the best battery configuration was founded for an electrode of MgH_2-$LiBH_4$-AB carbon and an electrolyte layer of $90LiBH_4+P_2S_5$ (initial specific capacity ~1000 mA h g^{-1}, 645.7 mAh g^{-1} after 10 cycles).

The thesis work was compiled in 6 chapters. Chapter 1, in this introductory chapter the importance of batteries was discussed. Focus on the importance of the development of next generation batteries and the benefits for the development of electronics applications, transportation, etc. the second part of this chapter present fundamentals related to the understanding of batteries operation. Then, metal hydrides as battery materials were reviewed. The objectives are described in Chapter 2. In Chapter 3, Materials and experimental methods for the preparation and characterization of battery composite materials used in this work are explained. Chapter 4 contains all the results. This chapter is divided in two sections. First section discussed the results when high temperature phase of $LiBH_4$ was stabilized with LiI at room temperature. Additionally, some battery configurations with $80Li_2S$-$20P_2S_5$ were analyzed. Same materials can be used mixed to prepare a different phase with a similar ionic conductivity. $LiBH_4$ with Li_2S and P_2S_5 was used to prepare $Li_6PS_5(BH_4)$. This alternative was discussed in the second section of Chapter 5. Finally, Chapter 6 compiles all the relevant references consulted during preparation of this work.