STUDY OF Li BEHAVIOUR IN ALL SOLID-STATE Li-S HALF CELL

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Abstract

The effect of a thin Ni barrier layer on Li diffusion - deposited between the solid electrolyte and the cathode - was investigated using Neutron Depth Profiling (NDP) and complemented by Rutherford Backscattering Spectrometry (RBS) for elemental depth distribution analysis. Half-cells consisting primarily of a LiPON solid-state electrolyte, MoS_2 cathode, and a top Au current collector were fabricated on Ti substrates via ion beam sputtering. Selected samples were prepared specifically to examine the potential impact of the Ni barrier on Li transport. While Ni is often proposed to suppress the shuttle effect in Li–S batteries, its influence on Li^+ ion diffusion remains poorly understood. The study showed that the Ni interlayer may hinder the diffusion of Li - S complexes between electrodes, suggesting a potential strategy to mitigate the shuttle effect and enhance Li - S battery performance. However, the observed effects are not yet conclusive and require further experimental validation.

Keywords: Energy storage systems, solid state half-cell, Li, sulfides

1. INTRODUCTION

The development of energy storage systems towards miniaturization represents a fundamental step necessary for their application in numerous fields where compact size is of critical importance and can significantly impact quality of life (e.g., in pacemakers and other implantable medical devices) [1]. Equally important is the reduction of costs and the overall waste of valuable materials and components that are difficult to recycle.

For the fabrication of thin batteries composed of multilayer structures, methodologies used in the preparation of nanolayers-commonly employed in microelectronics - can be advantageously utilized. However, in the case of thin-film batteries, it is essential that they deliver sufficient and long-term performance for practical applications. Given the limited amount of active material available in miniature battery systems, it is necessary to employ structural elements and their combinations that can achieve the desired battery parameters. One promising approach involves the use of unconventional Li-S combinations, which are considered a potential alternative to Li-ion systems due to the exceptionally high theoretical capacity of the sulfur cathode (exceeding 1600 mAh/g). Until now, Li-S systems have primarily been considered for high-performance batteries in large-scale formats using liquid electrolytes [2]. For their intended application in thin-film and miniature battery systems, it is first necessary to address a range of challenges associated with these electrochemistry units (e.g., poor conductivity and low sulfur utilization, dendrite formation and corrosion, the polysulfide shuttle effect, and volume expansion), all of which contribute to a reduction in the practical capacity of Li-S batteries despite their high theoretical energy density [3].

In this study, we focused on evaluation the possibility of influencing the transport of Li ions and Lipolysulfides in the electrolyte using an ultrathin layer of nickel, a promising ferroelectric material [4]. The aim of the experiment was to exploit the presence of nickel to suppress the shuttle effect, which is the main drawback responsible for the limited lifespan of Li-S systems. For the preparation of thin-film half-cells based on S and

Li, as well as for monitoring Li ion transport, nuclear analytical techniques available at NPI Řež - Neutron Depth Profiling and Rutherford Backscattering - were employed.

2. METHODOLOGY

Ti foils, 50 μm thick, were used as substrates and current collectors for the deposition of thin film half-cell system. A sketch of the investigated of 2 types of battery half-cells is shown in **Figure 1**. One can see that difference was just a presence of thin Ni barrier incorporated between the LIPO and MoS2 layers.

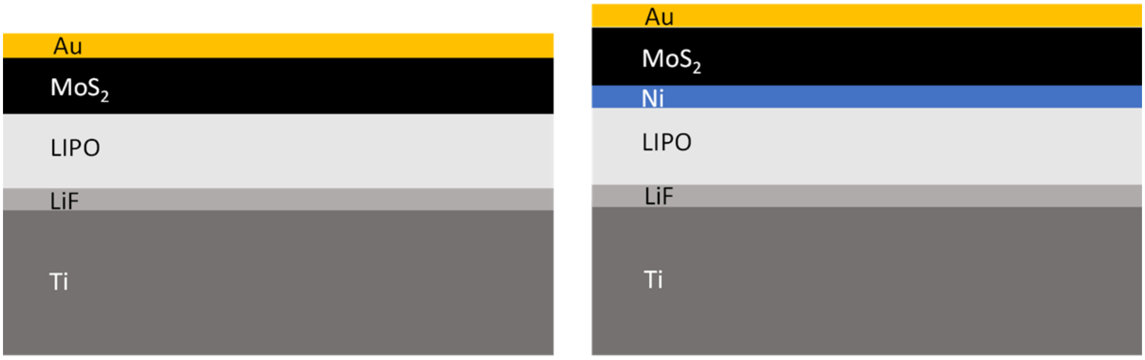


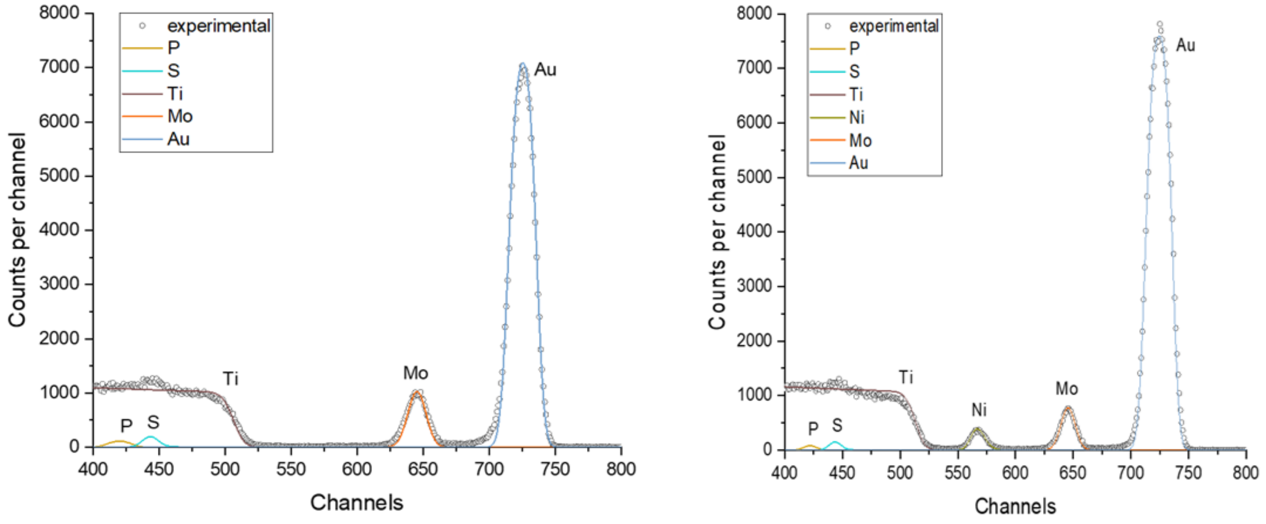
Figure 1 A schematic illustration of the two types of half-cell systems, which differ by the presence of a thin nickel barrier layer in one of the configurations.

To cover the surface with the multilayered thin films, a low energy ion facility (LEIF) was used. LEIF, generating an intense Ar ion beam with 20 keV energy and high current of 1 mA, was used to perform sputtering of high purity targets in high vacuum chamber. The Ar beam was focused on several targets placed on rotating holder in deposition chamber. For the experiment, two circular samples with the diameter of about 50.8 mm (2 inches) were prepared under the same experimental procedure (with the same geometry and ion beam parameters). The only difference was deposition of a Ni interlayer in one of the samples.

In order to study the elemental composition and the Li distribution, two complementary nuclear analytical technique were used, Rutherford Backscattering Spectroscopy (RBS) and Neutron Depth Profiling (NDP). The RBS measurements were carried out at the Tandetron MC 4130 accelerator in the NPI CANAM infrastructure [5]. In the experiment, He+ ions with an energy of 2 MeV and a low current of about 100 nA were used to avoid radiation damage to the structure of thin battery half-cells. NDP experiments were performed in LVR-15 research reactor (operated by the Research Center Řež) using a spectrometer of the NPI CANAM infrastructure. The samples were placed in vacuum chamber and irradiated through an aperture of 15 mm with thermal neutron beam of a 6E7 n/(cm^{2}s) neutron flux provided by supermirror neutron guide. Using thermal neutrons, a high cross section (940 b) nuclear reaction of (n,α) is induced on ^{6}Li isotope producing isotopically α (2055 kev) and T (2727 keV) charged particles. In both methods, the charged particles were detected using silicon detectors with high energy resolution (Canberra, 50 mm^2 sensitive area), energy spectra (registered with digitizers) were evaluated using commercial (SIMNRA, [6]) or lab/developed (LiBor, [7]) simulation codes.

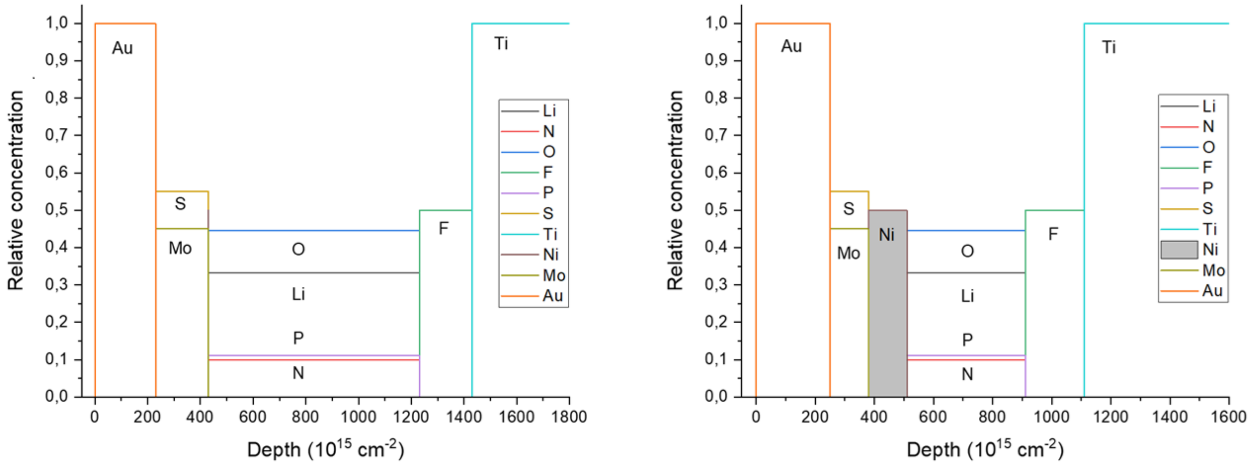
3. RESULTS

Figure 1 shows the RBS spectra (relevant range: 400–800 channels, corresponding to the distribution of the main constituent elements of the analyzed layers) measured for both of the above-mentioned configurations: Au/MoS_2/LiPON/LiF/Ti (**Figure 1a**) and Au/MoS_2/Ni/LiPON/LiF/Ti (**Figure 1b**). The spectra were evaluated using the SIMNRA code. **Figure 2** presents the resulting elemental depth profiles, which demonstrate that the samples were prepared with approximately the same relative composition. The only significant difference is the thickness of the LiPON interlayer: in the sample containing the Ni barrier, the LiPON thickness is approximately half that of the sample without Ni.



(a) (b)

Figure 2 RBS spectra with simulations of the samples Au/MoS_2/LiPON/LiF/Ti (a) and Au/MoS_2/Ni/LiPON/LiF/Ti (b).

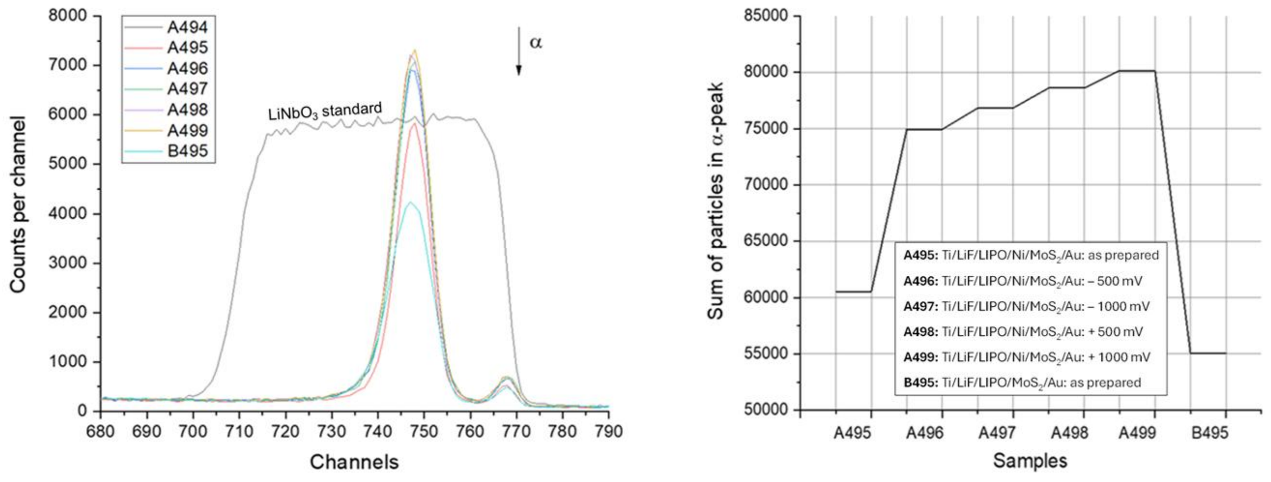


(a) (b)

Figure 3 Elemental depth profiles (relative concentration vers depth) of the samples Au/MoS_2/LiPON/LiF/Ti (a) and Au/MoS_2/Ni/LiPON/LiF/Ti (b).

Figure 4a shows the energy spectra of Li in samples subjected to bias voltages (−500 mV, -1000 mV, and +500 mV, +1000 mV) applied to the gold current collector. For the analysis, only the alpha particles from the reaction ^{6}Li(n,α)T were selected, as they are highly sensitive for assessing the depth distribution and diffusion of Li. In addition to measurements of the multilayer Li-S half-cells, the spectrum of a $LiNbO_3$ (417 nm) standard is also shown, enabling quantification of the absolute amount of Li migrating between the sample layers. As can be seen from the shape of the alpha peak, a small satellite appears near the nominal alpha edge position (~770 channels), which is attributed to Li ion diffusion toward the surface of the Au current collector. By comparing the ratios of the satellite and main peaks (R), it is possible to estimate the influence of the Ni barrier layer on the diffusion behavior of Li. It was found that for the sample with the Ni interlayer (A495), the ratio is R = 0.075, whereas for the sample without Ni (B495), it is R = 0.077. Although the difference between these ratios is relatively small (approximately 3%), likely due to the limited thickness of the Ni layer (70 × 10^{15} cm^{-2}), the results still suggest that Ni affects the diffusion of Li-S (polysulfide) complexes and may hinder their transport between electrodes. However, this effect must be verified through additional testing.

Figure 4b further presents the evaluation of NDP spectra, showing the areas of the main alpha peak (channels 730–760) for samples before and after exposure to negative and positive bias voltages. It is evident that in samples with the Ni layer, the area of the main peak increased by up to approximately 6% under both positive and negative bias. The fabricated multilayer structures were shown to be active, with free, diffusing Li ions. The increase in Li signal within the main peak can be explained by lateral diffusion of ions from regions outside the neutron beam footprint.



(a) (b)

Figure 4 (a) - NDP spectra of samples prepared with and without the Ni interlayer and subjected to positive and negative bias voltages (500 and 1000 mV); (b) - area of the alpha peaks (channel range 730–760) corresponding to the measured layers.

4. CONCLUSION

A pilot test using multilayer structures Ti/LiF/LiPON/Ni/MoS_2/Au and Ti/LiF/LiPON/MoS_2/Au (with and without Ni interlayer) demonstrated that (i) complex architectures with battery-active layers, responsive to applied voltage, can be successfully fabricated using ion beam sputtering, and (ii) the insertion of a thin Ni layer acts as a selective barrier, impeding the transport of Li ion complexes (such as polysulfides) while still allowing the passage of Li^+ ions. This result provides an initial indication that the development of Li-S systems with high potential for thin, high-performance batteries could benefit from the integration of ferroelectric thin-film filters that suppress the formation and migration of polysulfides, i.e., processes that otherwise lead to the rapid degradation of the thin Li-S battery systems. However, further verification of these findings is necessary.

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