

**Studies on the lithium ion diffusion coefficients of electrospun Nb₂O₅
nanostructures using galvanostatic intermediate titration and
electrochemical impedance spectroscopy**

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Abstract

We have studied the Li-diffusion co-efficient values of electrospun Nb₂O₅ nanofibers and nanonuggets for lithium batteries. In brief, Nb₂O₅ nanofibers were prepared by electrospinning followed by sintering at temperatures range 500-1100 °C for 1 h in air to obtain pseudo-hexagonal, orthorhombic (O), and monoclinic (M) Nb₂O₅ phases.. Electrochemical properties were evaluated by galvanostatic technique at room temperature. The H-, O- and M- Nb₂O₅ polymorphs delivered discharge capacities (at

second cycle) of 152, 189 and 242 (± 5) mAhg⁻¹, respectively. The lithium diffusion coefficients (D_{Li}) are calculated using Galvanostatic Intermittent Titration Technique (GITT) and Electrochemical impedance spectroscopy (EIS) techniques carried at room temperature. The evaluated D_{Li} values by GITT for H, O, and M-Nb₂O₅ phases are in the range 10⁻¹⁷-10⁻¹⁶, 10⁻¹⁵-10⁻¹⁴, and 10⁻¹³-10⁻¹² cm²s⁻¹ respectively, in the voltage range 1.0-2.6 V vs. Li. D_{Li} evaluated by EIS gave similar trend in the values but with a difference of one order higher magnitude.

Keywords : Li-diffusion co-efficient; Nb₂O₅ ; GITT; EIS ; SEM

1. Introduction

Binary and ternary oxides such as TiO₂, Li₄Ti₅O₁₂, V₂O₅, LiTiNbO₅, TiNb₂O₇, Nb₂O₅ and mixed oxides are shown to undergo intercalation and de-intercalation reaction [1]. Nb₂O₅ is used as an electrode material in lithium ion batteries commercialized by major companies including Panasonic and Sanyo. Nb₂O₅ could find applications in low voltage (2 V range) applications such as microelectronic or memory back up [2] systems. Different polymorphs of Nb₂O₅ compounds that have been studied are pseudo-hexagonal (H), orthorhombic (O), tetragonal (T), and monoclinic (M) [2, 3]. Kodama *et al.* [3] found that O-Nb₂O₅ particles possess superior cycling performance compared to M-Nb₂O₅ particles. In our previous work, we made an opposite observation in the case of bare and Ta-doped Nb₂O₅ nanofibers [4, 5]. Other groups studied the application of 1D nanostructure O-Nb₂O₅ in lithium batteries and report their high rate capability and stability [6, 7]. Previously Kugamai *et al.* [2] reported preliminary D_{Li} values for the three Nb₂O₅ polymorphs. It is crucial to investigate the morphology dependence Li-diffusion coefficients of electrospun H-, O- and M-Nb₂O₅ [2].

2. Experimental

Nb_2O_5 nanofibers were synthesized by electrospinning in a dedicated machine (Nanon, MECC, Japan). The solution for electrospinning was prepared from a mixture of 0.3 g of polyvinylpyrrolidone (PVP; $M_w = 1,300,000$, Sigma-Aldrich), 3.5 ml of absolute ethanol, 0.5 g of niobium ethoxide (Purity, 99.95%, Sigma Aldrich), and 1 ml of acetic acid. The solution was allowed to stir for 24 h before being loaded in a syringe. A 30 kV voltage was applied between the needle tip and a ground collector separated with a 10 cm distance to enable electrospinning. The obtained polymeric fibers were then heated in air in a box furnace (Carbolyte, UK) at 500 °C, 800 °C, and 1100 °C to remove the polymer and develop the desired crystal structure.

The morphology of the annealed fibers was characterized by Scanning Electron Microscopy (FE-SEM, JEOL JSM-5600LV). The crystal structure was probed by X-Ray Diffraction (Philips, X'PERT MPD, $\text{CuK}\alpha$ radiation) and lattice parameters were analyzed by TOPAS software. Density measurement was performed using pycnometer (AccuPyc 1330, Micromeritics) and BET surface area was evaluated by a surface area analyzer (Micromeritics Tristar 3000).

Electrodes for the Li-diffusion coefficient studies were prepared by mixing Nb_2O_5 nanostructures with carbon black and PVDF copolymer (binder, Kynar 2801) with weight percentage ratio 65: 20: 15 for H- Nb_2O_5 and O- Nb_2O_5 , and 70:15:15 for M- Nb_2O_5 . A slurry was prepared by dispersing the above component in N-methyl 2-pyrrolidinone, which was then deposited by the doctor blade technique as a ~ 20 μm thick layer on an etched copper foil. Circular electrode (area ~ 2 cm^2) was cut from the coated copper foil and more details on electrode fabrication are in our previous publications [8, 9]. The separator was a glass microfiber filter (Whatman) membrane, the counter and reference electrode was a 2 cm^2 circular piece of lithium metal. Coin-type test cells (CR2016) were fabricated in an Ar-filled

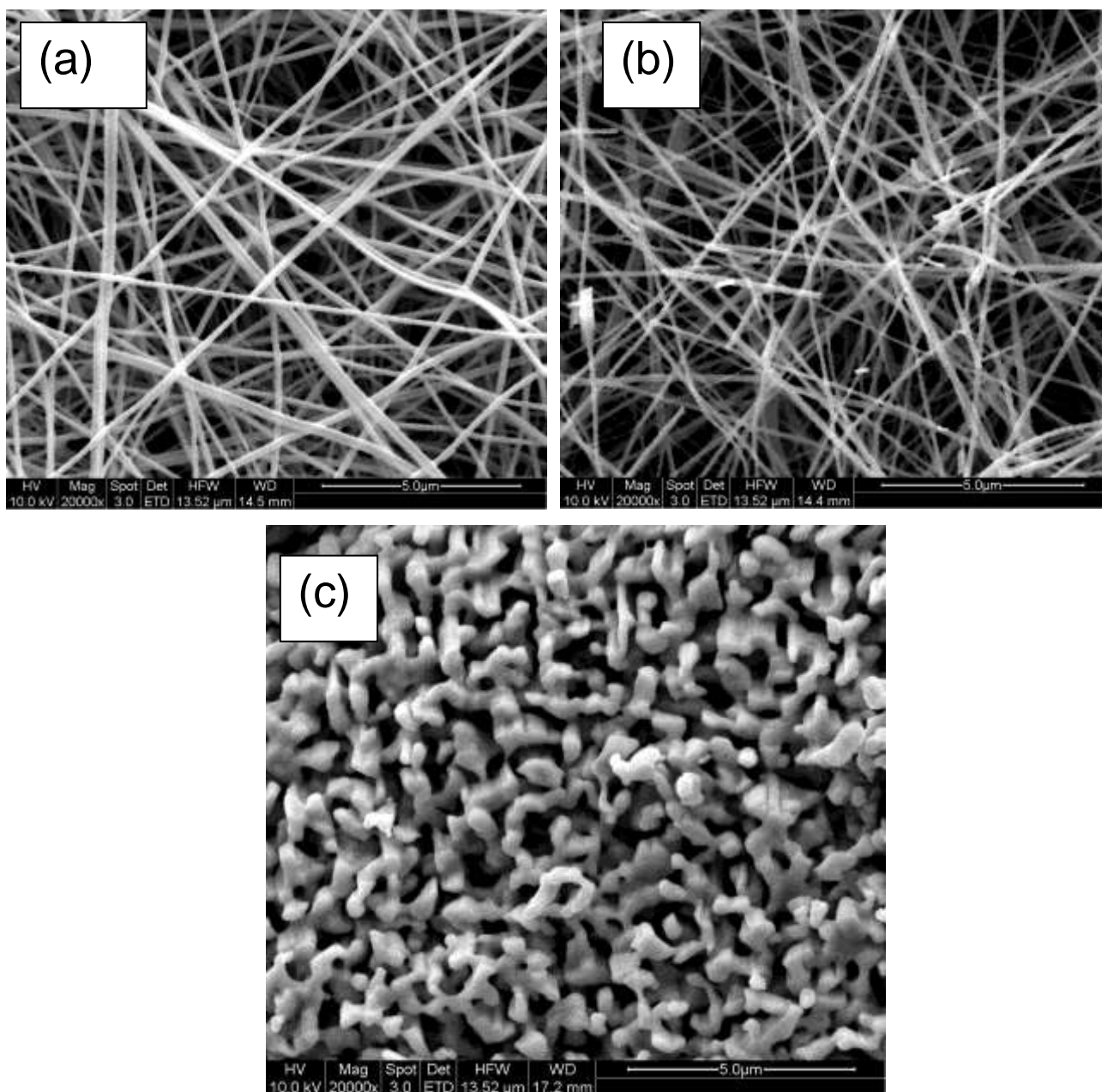


Figure 1. SEM images of Nb₂O₅ nanofibers sintered at (a) 500 °C, (b) 800 °C and (c) 1100 °C for 1 h in air ; magnification of 50 000x. Bar scale : 5μm.

glove box. Discharge-charge cycling and Galvanostatic Intermittent Titration Technique (GITT) were carried out using bitrode battery tester (Model SCN, USA). Electrochemical Impedance Spectroscopy (EIS) was carried out with solartron impedance/gain-phase analyzer

(model SI 1255) coupled with a potentiostat (SI 1268) at room temperature. The frequency was varied from 0.35 MHz to 3 mHz with an alternating current signal amplitude of 10 mV.

3. Results and discussion

The SEM images of Nb₂O₅ compounds are shown in Fig.1. As-spun polymeric fibers had a diameter ~ 300 nm. Upon sintering up to ~450 °C, PVP evaporated and the fiber diameter reduced to ~160 nm [4]. The diameter remained constant at temperature up to 900 °C but the fiber surface changed from a smooth surface at 500 °C (Fig.1a.) to an uneven surface at 800 °C (Fig.1b.). At higher temperatures, the fiber morphology was distorted into a nugget-like shape (Fig.1c.) with irregular and increased average diameter. XRD analysis of the annealed sample allowed identifying the crystal structures of the 500 °C, 800 °C, and 1100 °C annealed samples to be pseudo-hexagonal (P6/mmm space group), orthorhombic (pbam space group), and monoclinic (P12/m1 space group), respectively. More detailed analysis are available in our previous publication [4].

Cyclic voltammetry and galvanostatic cycling studies of cells based on H-, O-, and M-Nb₂O₅ had already discussed in our previous publication [4]. For clarity and discussion for Li-diffusion coefficients studies, we have shown galvanostatic cycling curves of H-, O-, M-Nb₂O₅ in the Figure 2, which were cycled in the voltage range, 1.0 – 2.6 V and at a current of 50 mA g⁻¹ at room temperature. The H-, O- and M-Nb₂O₅ polymorphs delivered at second cycle discharge capacities of 152, 189, and 242 (±5) mAh g⁻¹, respectively. The corresponding capacity fading between the 2nd and the 30th cycle were 22, 40 and 12%, respectively. The reversible capacity and shapes of cycling curves increased with the sintering temperature. The capacity fading was higher for O- Nb₂O₅ and lowest for the M-Nb₂O₅. To investigate the difference in cycling performance, we performed galvanostatic

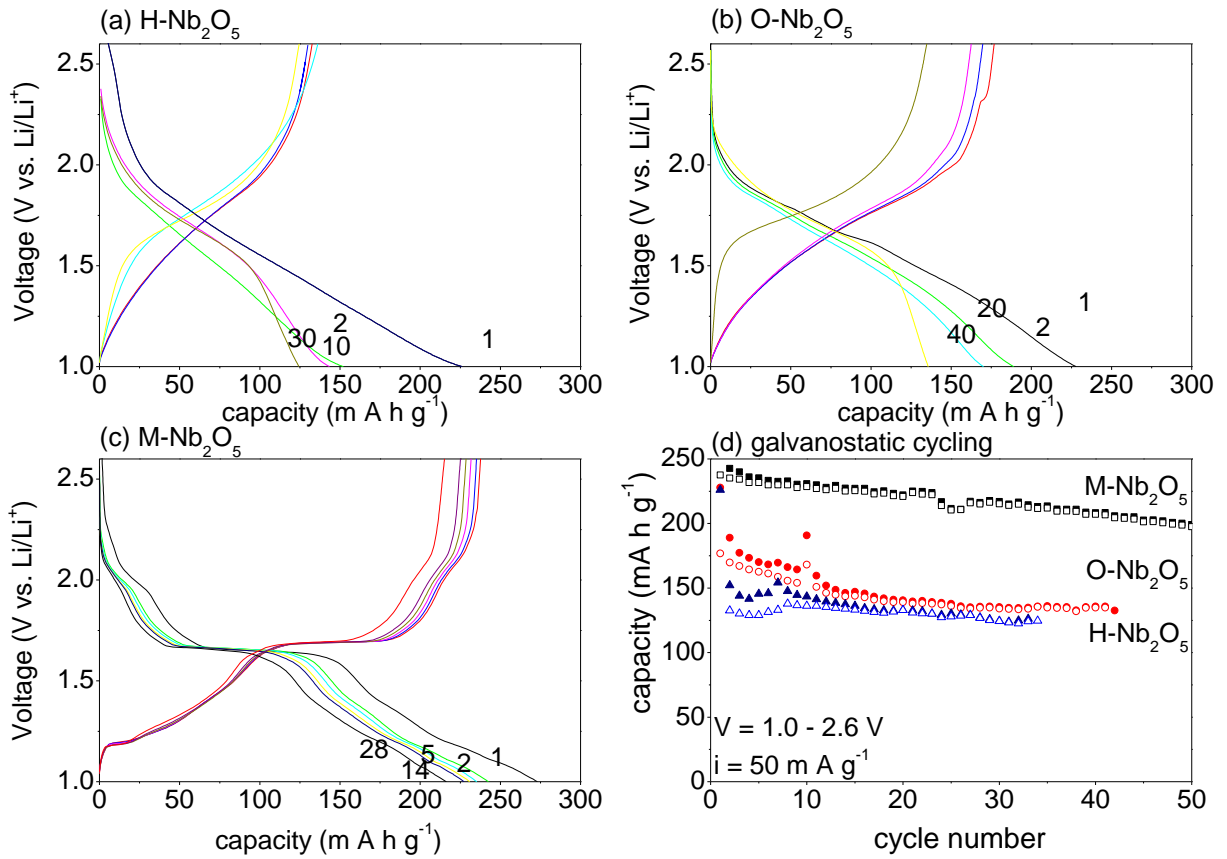


Figure 2. Galvanostatic cycling of cells, Voltage vs. capacity plots of (a) H-Nb₂O₅, (b) O-Nb₂O₅, and (c) M-Nb₂O₅ in the voltage range 1.0 – 2.6 V and with a current rate of 50 mA g⁻¹ at room temperature ; (d) Capacity vs. cycle number of H-Nb₂O₅, O-Nb₂O₅, and M-Nb₂O₅.

intermediate titration (GITT) and electrochemical impedance spectroscopy (EIS) of H, O, M-Nb₂O₅ nanostructures.

GITT is a useful and well adopted technique to calculate the Li-diffusion coefficients of intercalated/de-intercalated compounds [10, 11]. In this technique, the cell voltage is then perturbed by charging or discharging at a constant current. The cell potential is then allowed to relax for long time (~5 h). The diffusion coefficient can be evaluated from the voltage relaxation characteristic relative to its anterior perturbation. From an initial steady

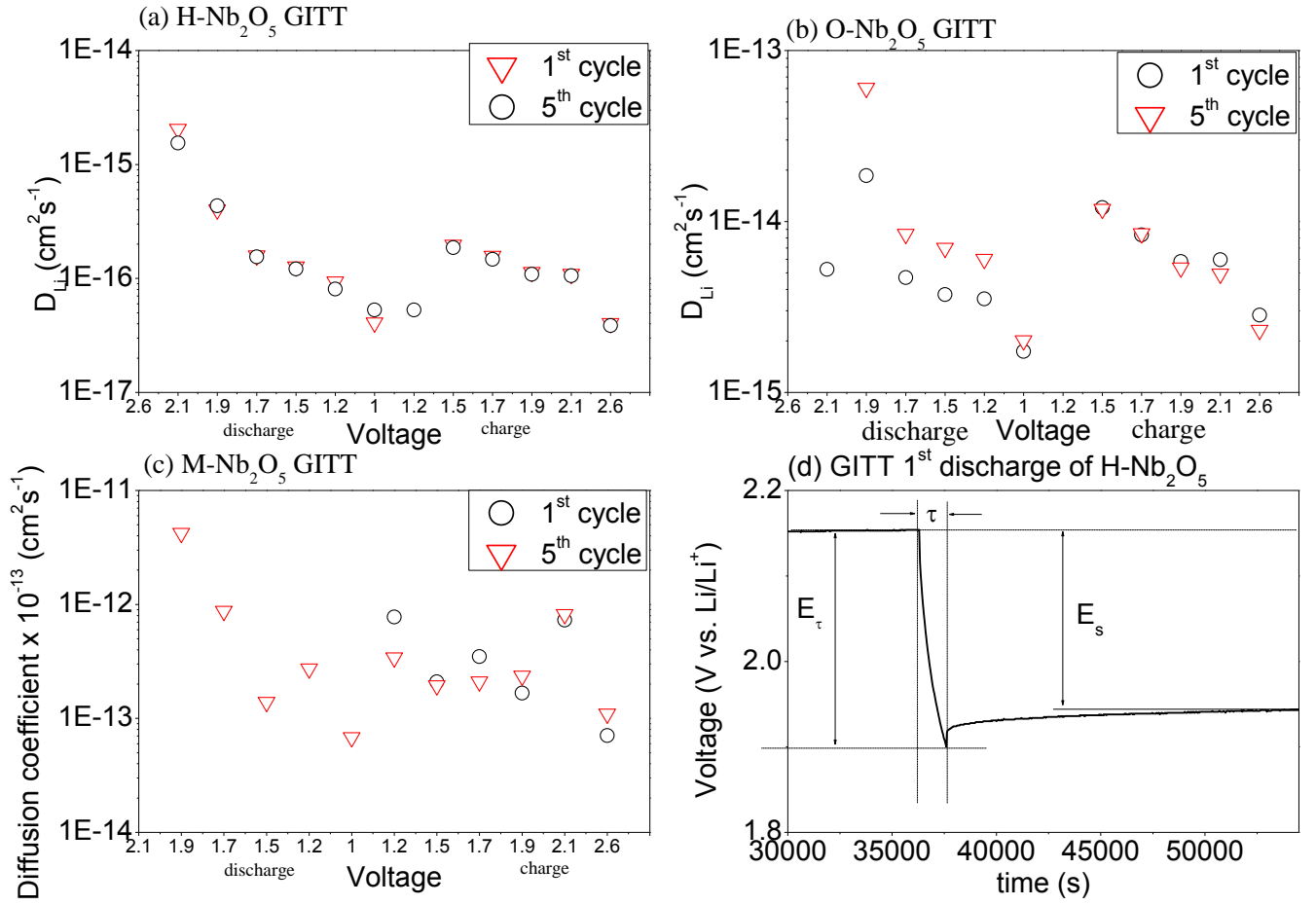


Figure 3. Diffusion coefficient calculated with GITT measurement from cells of (a) H-Nb₂O₅, (b) O-Nb₂O₅, and (c) M-Nb₂O₅; (d) GITT curve (voltage vs. time) of the H-Nb₂O₅ during first discharge at 1.9 V.

state with a voltage E_s , the cell charges/discharges for a duration “ t ” inducing a change “ ΔE_s ” in the voltage. Then the cell rests until a new steady state is reached, with a potential E_0 (Fig. 3). If “ ΔE_s ” is the change in the steady state potential before and after the charge/discharge ($\Delta E_s = E_0 - E_s$), the Li- diffusion coefficient is calculated as:

$$D_{Li} = \frac{4}{\pi} \left(\frac{m_B V_m}{M_B A} \right)^2 \left(\frac{\Delta E_s}{\tau \frac{dE_\tau}{d\sqrt{\tau}}} \right)^2 \quad \tau \ll \frac{L^2}{D_{Li}}$$

where m_B is the active mass in the electrode, V_m is the molar volume of the compound, the relative formula mass, and A is the area between the electrolyte and the active material. In literature, A can be considered by different ways like assuming the geometrical area of the electrode or using BET surface area measurements. In our present calculation, “ A ” was evaluated from BET surface area and the mass of active material. D_{Li} was calculated during the first and fifth cycle, during discharge and charge at the following potential: 2.1, 1.9, 1.7, 1.5, 1.2, 1.0 V vs. Li, (discharge): 1.2, 1.5, 1.7, 1.9, 2.1, 2.6 V vs. Li. The D_{Li} values for the H-, O-, M-Nb₂O₅ are displayed in Figure 3. D_{Li} during the first cycle for H-, O- and M-Nb₂O₅ were in the range 10^{-17} - 10^{-15} , 10^{-15} - 10^{-13} , and 10^{-13} - 10^{-11} cm² s⁻¹, respectively (Fig. 3). The D_{Li} values during the 5th cycle discharge cycle are almost similar to first cycle (Fig. 3). The diffusion coefficient increased with the sintering temperature, by increase of two order of magnitude from H- to O- and from O- to M-Nb₂O₅. These values are in agreement with the observed variation of galvanostatic cycling results (Fig. 2).

To confirm GITT observations, complementary Electrochemical Impedance Spectroscopy (EIS) analysis was performed on cells based on the three polymorphs. During EIS studies, the cell is subjected to a small sinusoidal perturbation and the response recorded both in amplitude and phase. If the frequency range of the sinusoid input is large, EIS spectra may reveal lot of information about the physical processes occurring in a cell, This is because EIS can separate process with different time constant. At high frequency, semi circles in the cole-cole plot are characteristic of charge transfer mechanism, as well as surface film and bulk material related process[12, 13]. At lower frequencies, straight line inclined at 45° roots from diffusion of lithium into the active material. In this region, D_{Li} can be calculated as the

Warburg impedance Z_w is inversely proportional to the square root of the diffusion coefficient as shown in [14].

$$D_{Li} = \frac{1}{2} \left(\frac{V_m}{FA\sigma} \right)^2 \left(\frac{dE}{d\delta} \right)^2$$

where F the Faraday constant, σ the Warburg factor ($\Omega \text{ Hz}^{-1/2}$), and $dE/d\delta$ the slope of the electrode potential (E) in function of the composition (δ). D_{Li} from EIS was calculated for the three polymorphs during the 1st and the 5th cycle, at the same voltage as the GITT. Figure 4(d) shows an example of an EIS spectrum featuring a Warburg region with a 45° slope in the low frequency region. D_{Li} values during the first cycle for H-, O- and M-Nb₂O₅ were calculated to be in the 10^{-16} - 10^{-14} , 10^{-15} - 10^{-12} , and 10^{-12} - $10^{-10} \text{ cm}^2 \text{ s}^{-1}$ range, respectively. During the fifth cycle, D_{Li} values were similar to the 1st cycle for H- and M- Nb₂O₅, but for the D_{Li} of O- Nb₂O₅ were lower by an order of magnitude when compared to the first cycle. This decrease in D_{Li} corroborates the high capacity fading found in O-Nb₂O₅ compared to the two other polymorphs. EIS provided D_{Li} values with similar trend compared to GITT, as D_{Li} values are of two orders of magnitude higher in M- than O-, and in O- than H- Nb₂O₅. However, the D_{Li} values differ by an order of magnitude between GITT and EIS measurements. The difference is expected to arise from the uncertainties inherent to both techniques. In GITT, the perturbation time should be long enough to provide a measurable and accurate response, but should be short compared to the characteristic diffusion time [14]. If the charge or discharge is too large, the diffusion coefficient values lose in precision. The uncertainty in D_{Li} values comes from the differences in identifying the Warburg region. If the time constant of the different processes in a battery are too close, the impedances arising from

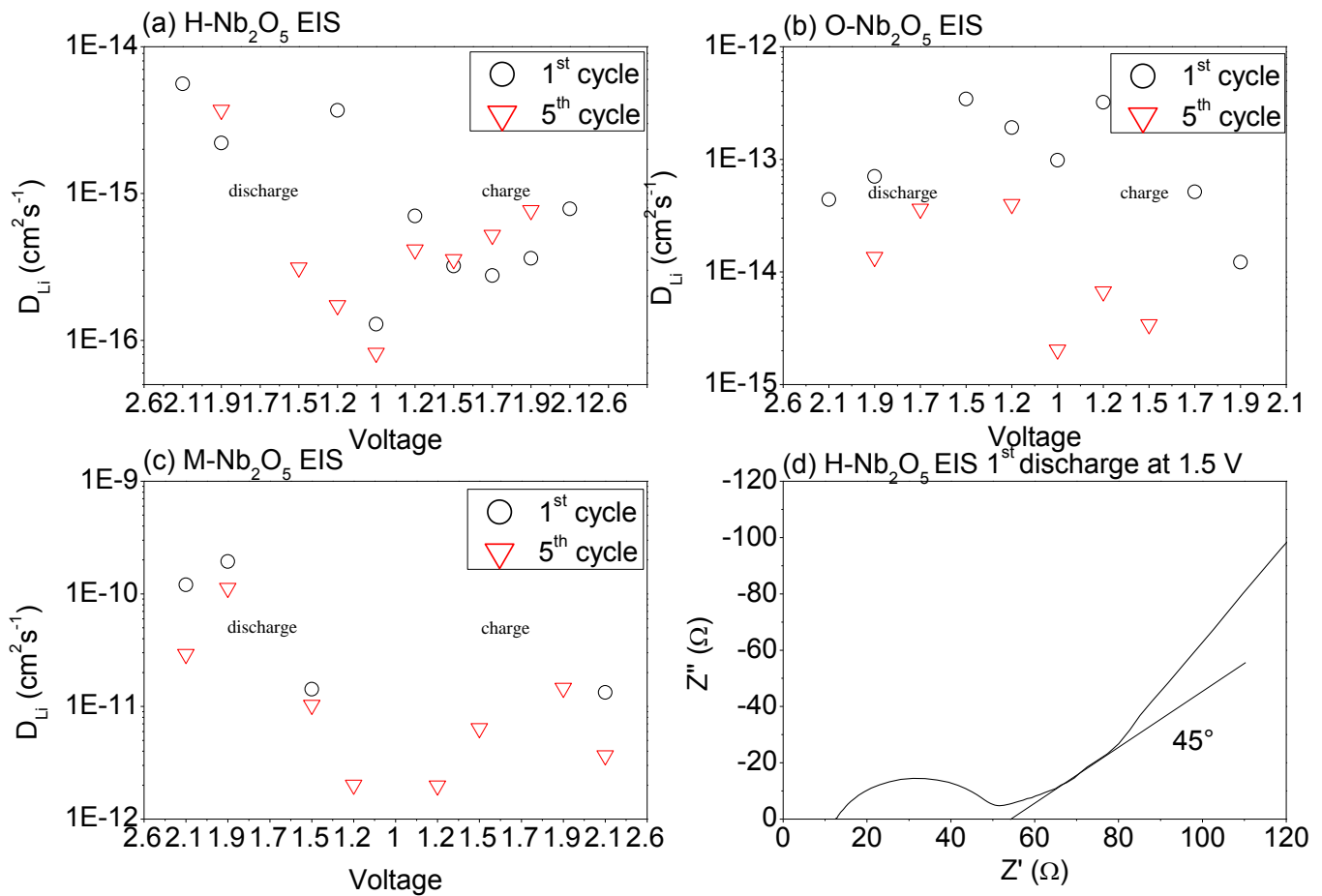


Figure 4. Li-diffusion coefficient values calculated from EIS measurement of the cells (a) H- Nb₂O₅, (b) O- Nb₂O₅, and (c) M-Nb₂O₅ ; (d) Nyquist plots (Z' vs. $-Z''$) of the H-Nb₂O₅ during first discharge at 1.5V featuring a Warburg region with a 45° slop.

these phenomena overlap and likely to hide the Warburg region. In literature reported the differences in diffusion coefficient values from calculated from GITT and EIS or cyclic voltammetry techniques [15]. Li-diffusion coefficient value of Nb₂O₅ particles has been studied by Kumagai et al. by the current pulse relaxation technique [2]. They reported D_{Li} values are in the range, 10^{-11} - 10^{-10} cm^2s^{-1} for H-, O-, and M-Nb₂O₅, with values lower for M-, compared to H- and O-Nb₂O₅. These values confirm their observation of lower cycling

performance of M-Nb₂O₅ compared to the other polymorphs. It can be noticed that Kugamai *et al*[2] reported similar range of D_{Li} values for the three polymorphs, whereas this study reports large difference for the D_{Li} values from one structure to another and also come from the assumption made in “A” values of the calculation of D_{Li}. In GITT, the Warburg prefactor technique or the current pulse technique, D_{Li} is inversely proportional to the square of the surface area. Kodama *et al.* assumed ‘A’ to be equal to the geometrical area of the electrode whereas the present study calculated it from the BET analysis.

4. Conclusions

Nb₂O₅ nanofibers/nanonuggets were synthesized by electrospinning and applied in lithium battery. The H-, O- and M-Nb₂O₅ polymorphs delivered at second cycle discharge capacities of 152, 189, and 242 mA h g⁻¹, respectively. The corresponding capacity fading between the 2nd and the 30th cycle were 22, 40 and 12%, respectively. Diffusion coefficients in these three polymorphs were calculated during different cycles and at different voltages, by GITT and EIS techniques. The values from GITT for H-, O-, and M-Nb₂O₅ are in the range 10⁻¹⁶-10⁻¹⁴, 10⁻¹⁵-10⁻¹², and 10⁻¹²-10⁻¹⁰ Cm² s⁻¹, respectively. The calculated D_{Li} values from impedance studies showed similar trend, with higher values by an order of magnitude. The D_{Li} studies confirmed the superior cycling performance of Nb₂O₅ nanonuggets over the H- and O-Nb₂O₅ nanofibers.

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