In-situ Li Redistribution Detection and Indirect Probing of Li Dendrite in $Li_7La_3Zr_2O_{12}$ Upon Electrochemical Cycling by ^{7}Li Magnetic Resonance Imaging

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Introduction

The formation of Li dendrites in solid electrolytes is the cause of failure of battery operation. [1] Therefore, it is important to understand the correlation of Li dendrite formation with Li-redistribution under cycling conditions. ^{7}Li MRI has been proven to be useful in detecting Li-redistribution at electrode-electrolyte interfaces.[2] Here, we employ *in situ* ^{7}Li MRI monitoring of changes in Li distribution at different electrochemical cycling stages in $Li_7La_3Zr_2O_{12}$. The dendrite formation is correlated with electrochemical cycling profiles and ^{7}Li concentration mappings across the solid electrolyte.

Experimental

The cycling of a symmetric cell with Li metal as the electrode and $Li_7La_3Zr_2O_{12}$ as the electrolyte was finished by a Gamry Reference 600+ (Warminster, PA) with a constant current density for each charging/discharging cycle, which gradually increased from 10 μA/cm^2 to 360 μA/cm^2. ^{7}Li (ω_0 = 394.7 MHz). 2D FLASH MR images with a 200-μm isotropic resolution were collected before and after each step of charge or discharge in a 21.1-T ultra-wide bore magnet at the NHMFL. The flip angle was set to 30° and the partial fourier techniques were used. Echo time (TE)/repetition time (TR) = 0.9/300 ms were employed. 3D ^{7}Li MR images were acquired at 11.75 T (Magnex Scientific, Oxford, UK) at FAMU-FSU College of Engineering with 100-μm isotropic using TE/TR=1 /250 ms. The images were processed with ImageJ (NIH Bethesda, MD).

Results and Discussion

To visualize the Li concentration/spin density changes across layers, the intensity of each layer from top (#1) to bottom (#6) of a solid pellet was integrated and plotted during cycling in **Fig. 1**. With small current density (0-2 h), the redistribution of Li across layers was minimal. As the current density was increased (4-6 h), the layers close to electrodes (#2/5) suffered from Li deficiency and large voltage polarization. After the short-circuit due to the formation of dendrites around 6 hours, the total ^{7}Li intensity began to drop. The Li deficiency became more severe at layers #2/5 followed by layers #3/4, which agreed with the dendrite growth from top/bottom to middle layers. The comparison between cross sections taken from 3D MR Image and pictures taken on sanded solid electrolyte is shown in **Fig. 2**, where vacant spots in MRI matched with actual dark spots of Li dendrite indicated by red arrows. This suggests that Li dendrites in 3D solid electrolytes can be indirectly observed with MRI.

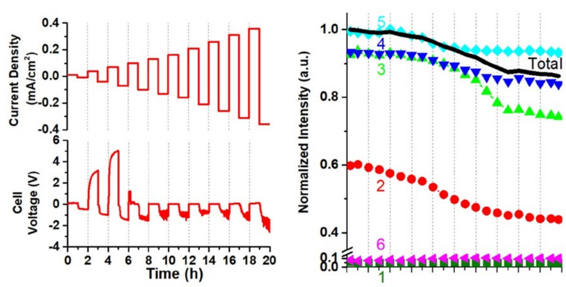

Fig 1. The electrochemical change and the intensity of different layers in LLZO pellet during cycling of the battery.

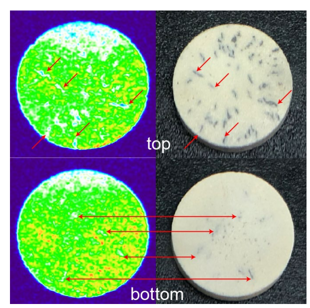

Fig 2. 2D cross-sections of top and bottom layer v.s. real image of the LLZO pellet.

Conclusions

The Li redistribution upon electrochemical cycling was detected in real time using ^{7}Li MRI and the intensity changing trend among different layers was well correlated with the dendrite formation in Li/LLZO/Li battery. Given the relationship between Li ion deficiency and Li dendrite formation, the position of dendrite can be determined indirectly, indicating the potential of MRI as a powerful tool to characterize the failure of all-solid-state Li-ion batteries.

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References

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[2] Chien, P.H., *et al.*, J. Phys. Chem. Lett., **9(8)**, 1990-1998 (2018).