***In situ* ^7Li and ^{133}Cs Nuclear Magnetic Resonance Investigations on the Role of Cs^+
Additive in Lithium-Metal Deposition Process**

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Abstract

Cesium ion (Cs^+) has been reported to be an effective electrolyte additive to suppress Li dendrite growth which prevents the application of lithium (Li) metal as an anode for rechargeable Li batteries. In this work, we investigated the effect of Cs^+ additive on Li depositions using quantitative *in situ* ^7Li and ^{133}Cs nuclear magnetic resonance (NMR) with planar symmetric Li cells. It's found that the addition of Cs^+ can significantly enhance both the formation of well aligned Li nanorods and reversibility of the Li electrode. *In situ* ^{133}Cs NMR directly confirms that Cs^+ migrates to Li electrode to form a positively charged electrostatic shield during the charging process. Much more electrochemical “active” Li was found in Li films deposited with Cs^+ additive, while more electrochemical “dead” and thicker Li rods were identified in Li films deposited without Cs^+ . Combining the *in situ* and the previous *ex-situ* results, a Li deposition model has been proposed to explain these observations.

Keywords: batteries, cesium ion, lithium, in situ, NMR

Introduction

Lithium (Li) batteries with high energy density and power capability have been widely used in modern portable electronic devices. Their extended applications in larger scale energy storage for transportation systems such as electric vehicles have been greatly demanded as energy and environmental issues from traditional fossil fuels become increasingly an international concern.[1-3] Compared with commercial graphite anode, Li metal anode has attracted great interests for its extremely high theoretic specific capacity (3860 mAh.g^{-1}) and the lowest electrochemical reduction potential ($-3.04 \text{ V vs. Li/Li}^+$).[1] However, the application of Li metal anode has been hindered by two serious problems: 1. the dendrite growth. 2. “dead” Li formed on Li anode which is related to the low Coulombic efficiency over repeated charge-discharge cycles.[4] Thus, considerable efforts have been taken to understand and prevent the formation of these microstructures.[4-9] Generally, dendrite growth can be suppressed by various electrolyte additives to form a uniform solid electrolyte interface (SEI), or by forming alloys with Li metal during Li deposition process to stabilize Li electrode.[10-14]

Recently, a new approach was proposed to suppress Li dendrite growth based on a self-healing electrostatic shield (SHES) mechanism. This approach used low concentration Cs^+ or Rb^+ in base electrolyte (1M LiPF_6 in propylene carbonate (PC)) to form a positively charged electrostatic shield around the initial grown Li tips or protuberances and force further deposition of Li to adjacent regions on the anode.[15] Low concentration Cs^+ or Rb^+ added in the base electrolyte can significantly change the morphology of deposited Li film and form dendrite-free Li films.[15, 16] In fact, further detailed investigations by cross section scanning electron microscopy (SEM) indicate that the dendrite-free Li film is composed of self-aligned and highly compacted nanorod microstructures. SEM images, X-ray photoelectron spectroscopy (XPS),

electrochemical analysis combined with theoretic simulations suggest that smooth Li deposition in Cs^+ -containing electrolyte is the result of a synergistic effect of Cs^+ additive and preformed SEI layer.[17] However, *in situ* or *operando* evidences for supporting the proposed role of Cs^+ are still lacking since all prior investigations use *ex situ* techniques.

In situ characterization methods such as optical microscopy and SEM have been employed to obtain the morphology information on dendrite growth during battery cycling process, but these methods suffer from lack of quantitative information.[4, 5] *Ex situ* $^7\text{Li}/^6\text{Li}$ NMR is a routine and powerful tool to obtain the quantitative information of different environmental Li species from electrolyte to electrode in Li batteries.[18-20] *In situ* ^7Li NMR technique has been nicely established to probe real-time, dynamic, and quantitative information of Li batteries under their working conditions.[21-23] For example, Li intercalation and de-intercalation processes in graphite electrode were monitored by *in situ* ^7Li NMR with quantitative information on both the Li-graphite intercalation products and the deposited Li-dendrite obtained.[24] Bhattacharyya *et al.*, utilized *in situ* ^7Li NMR to directly obtain time-resolved, quantitative information about dendritic/mossy Li deposited on Li electrode with cycling proceeding.[25] For these *in situ* NMR studies, the chemical shift of Li metal was found to be sensitive to the relative orientation between the metal surface and the magnetic field $\mathbf{B}_0$ due to the bulk magnetic susceptibility (BMS) effect, and the chemical shift of metallic Li can change from 242 to 272 ppm by varying Li stripe from perpendicular to parallel to the magnetic field.[26] However, until now the quantitative information of Li microstructures is only derived from the normalized total signal changes of Li metal from 240 to 280 ppm without differentiating the orientation dependent Li metal signals. Valuable information may exist in this chemical shift range for us to extract the detailed Li-deposition behavior at the Li-metal electrode during battery cycling process.

In this work, planar symmetric Li metal cells (i.e. Li|Li) with and without Cs^+ additive were fabricated and investigated by *in situ* ^7Li and ^{133}Cs NMR. The effect of Cs^+ on Li deposition behavior was investigated by separating the Li metal signals with respect to their orientations to $\mathbf{B}_0$, which is the first time report. The role of Cs^+ was directly followed by *in situ* ^{133}Cs NMR. At last, a new lithium deposition model was proposed to explain the observed NMR results.

Experimental

All the *in situ* ^7Li and ^{133}Cs single pulse NMR experiments were performed on a Varian 300 MHz NMR spectrometer with the Larmor frequencies of 116.58 MHz and 39.35 MHz for ^7Li and ^{133}Cs , respectively. A home made *in situ* ^7Li NMR probe (Figure 1a) with a 5-turn solenoid RF coil (ID of 12 mm) with the excitation magnetic field ($\mathbf{B}_1$) perpendicular to the main magnetic field ($\mathbf{B}_0$) was used for the measurement. 1 M LiCl aqueous solution was used as the reference (0 ppm). Each spectrum was acquired using a single pulse with flip angle of 45° , an acquisition time of 50 ms, a recycle delay time of 1s, and a total accumulation number of 256. The cells were cycled consecutively from 0.1 mA, 0.25 mA to 0.5 mA (i.e., 0.2, 0.51, 1.0 mA cm^{-2}), and for each constant charge-discharge current, 500 individual spectra were acquired. For the *in situ* ^{133}Cs NMR, a 8-turn solenoid RF coil (ID of 12 mm) with the excitation magnetic field ($\mathbf{B}_1$) perpendicular to the main magnetic field ($\mathbf{B}_0$) was used for the measurement of the Li-metal cells with Cs^+ additive.

The design of the *in situ* NMR cells is illustrated in Figure 1b, and the cells were symmetrically fabricated by two flat Li metal foils (7 mm long $\times$ 7 mm wide $\times$ 0.75 mm thick, Alfa Aesar) separated by a flat glass fiber (0.75 mm thick, Whatman GF/B) separator. Propylene carbonate (PC) was used as the solvent in testing electrolytes since it has better dissolution to

CsPF₆. The cell was inserted into a specially designed *in situ* NMR cell capsule case made of Kel-F. The capsule case contains a main cylinder holder (OD of 12 mm) with a rectangular prism void, and a Kel-F cap that fitted into the cylinder holder as illustrated in Figure 1c. A center hole of about 1 mm in ID was drilled for guiding the two electric wires (Cu wires with a diameter of 0.05 mm that were imbedded into the two Li-metal electrodes) to the outside of the cell for charging and discharging *via* a CHI600D electrochemical workstation (CH Instrument). The cap was glued to the main body of the cylindrical cylinder and the center hole was sealed using epoxy to prevent the leakage of the electrolytes as well as to prevent the exposure of the battery to air. In this work, the same electric charges for deposition and stripping processes were used, which was the condition to completely strip the deposited Li during discharge process.

LiPF₆ and PC were purchased from Novolyte in battery grade. AgPF₆ and CsI (99.999%) were ordered from Sigma-Aldrich. CsPF₆ was synthesized by mixing stoichiometric amounts of AgPF₆ and CsI in PC solution inside a glovebox (MBRAUN) filled with purified argon where the oxygen and moisture content was less than 1 ppm, followed by filtration of the formed AgI from the solution by using 0.45 μm syringe filters. LiPF₆ was then added into the CsPF₆-PC solution to obtain the electrolyte with 1 M LiPF₆ and 50 mM CsPF₆. For the symmetric Li-metal cell without Cs⁺ additive, the 1 M LiPF₆-PC electrolyte was used in assembling the *in situ* NMR battery.

Results and Discussion

Selected *in situ* ⁷Li NMR spectra of the Li|Li symmetric cells with and without Cs⁺ additive at different charge-discharge currents are shown in Figure 2 (note that the *in situ* experiments

were carried out sequentially from 0.1 mA to 0.5 mA). The pristine (i.e., before discharge-charge) cells with (Figure 2a') and without (Figure 2a) Cs^+ show one major peak near 248 ppm and a weak shoulder peak at about 260 ppm. Although NMR signals from both electrodes in Li|Li symmetric cell have been collected in this work, for convenience of expression, we define the Li electrode which received the initial Li deposition as anode, while define the Li electrode which was stripped of Li as cathode. We also define the initial Li transfer process shown in Figure 2I and Figure 2II as charge process, and the reversed process as the discharge process. Both the 248 and the ~260 ppm peaks are from Li metal electrodes and the chemical shift difference is due to bulk magnetic susceptibility (BMS) effect arising from different orientations of the Li metal surfaces.[26] In order to accurately explain the chemical shifts, we measured the orientation dependent major ^7Li NMR peak as a function of the normal direction of the Li-metal foil surface with respect to the main magnetic field ($\mathbf{B}_0$) and the results are summarized in Figure S2 and Table S1 in the Supporting Information. The results indicate: (i) the chemical shift of Li-metal signal changes from about 244 ppm for the Li foil surface perpendicular to $\mathbf{B}_0$, to about 273 ppm corresponding to the Li foil surface parallel to $\mathbf{B}_0$; (ii) the integration of the peak area is fairly constant with no more than 10% of the total signal change over a full rotation, and (iii) the linewidth of the major peak also changes only marginally on the orientation of the Li-metal surface, i.e., about 595 and 782 Hz. The minor variation of signal intensities may result from the small deviation of relative angle between radio frequency (rf) and Li foil while the linewidth changes can be attributed to the difference in main field homogeneity changes when the foil rotates to a different orientation.[27] Based on the results from Figure S2, the 248 ppm peaks (Figure 2a, 2a') are attributed to Li metal signal near the major electrode surface due to the skin effect (approximately 15 μm depth at 4.7 T magnetic field), and the corresponding normal

direction of Li-metal electrode is about 20° away from to $\mathbf{B}_0$. The ~ 260 ppm shoulder peak (Figure 2a, 2a') is the signal arising from the edge of the Li foil and the uneven surface of Li metal foil mainly exhibiting angles about 40° to 50° with respect to the $\mathbf{B}_0$. During cycling at 0.1 mA, a new peak centered at about 267 ppm appears in the spectra of both cells (Figure 2b-d and 2b'-d'). This peak corresponds to the deposited Li metal microstructures with the average normal direction of the surface oriented approximately 120° to $\mathbf{B}_0$. Since the Li-metal electrode surface is oriented about 20° with respect to $\mathbf{B}_0$, then the average surface of the deposited microstructured Li-metal is almost oriented perpendicular to the Li-metal electrode surface. When the charge current is increased to 0.25 mA, the signal near 267 ppm increases significantly for both cells over the charging process (Figure 2e'-f' and 2e-f), while it decreases substantially for the cell with Cs^+ over the discharging process (Figure 2g' and 2g). However, after the 2nd charge the peak increase more significantly for the cell with Cs^+ (Figure 2h' and 2h). It means the formation of this kind of microstructure at 267 ppm is more significant, but it has better reversibility during cycling process when Cs^+ was added. With cycling current increased to 0.5 mA, the signal intensity of 267 ppm peak increases much more significantly for both cells, but the intensity decrease during discharge process is not obvious (Figure 2i-l and 2i'-l'). The effect of Cs^+ exhibits at moderate cycling current (0.25 mA), because very small amount of micro-structured Li was formed at lower cycling current (0.1 mA), while at much higher cycling current (0.5 mA), the effect of Cs^+ on the protection of Li metal electrode is significantly reduced.[28] It should be pointed out that even though the discharge condition for complete stripping was used, there might be some parts of the deposited Li remaining on the Li metal electrode and the Li stripping from the Li metal electrode might occur.

Quantitative analysis of the *in situ* ^7Li NMR spectra as a function of charge-discharge time was conducted to gain more dynamic and quantitative information on the microstructure changes near the electrode during cycling process. The normalized total signal intensities (see supporting information for details) of Li-metal during cycling process at different currents are shown in Figure 3, which reflect the total amount of microstructures formed during the cycling process for the symmetric cells.[25] It is seen from the charge/discharge curves for the Li|Li cells containing electrolytes with and without Cs^+ in Figure 3 that the Cs^+ -containing electrolyte leads to higher ohmic resistances than the control electrolyte does. This is because the Cs^+ cations form positively charged electrostatic shield on Li metal surface thus increase the Li^+ ion transfer resistance, as indicated in the previous report.[16] It should be pointed out that the polarity of the potential associated with the two Li electrodes will be switched during charge and discharge process, and Cs^+ will form the electrostatic shield at corresponding electrode due to the electrostatic forces. Indeed, the beginning shape of the discharge profile between the cell with Cs^+ additive is different from that without Cs^+ additive as is evident for the 0.25 mA case (Figure 3b and 3b'). The cell with Cs^+ additive shows a linear increase of the signal intensity during charge process even at low current of 0.1 mA (Figure 3a'), while there is no obvious change for the cell without Cs^+ (Figure 3a). Based on cross-section SEM results that the microstructures of deposited Li film are mostly composed of highly ordered compacted Li nanorods with the diameter smaller than 1 μm (See supporting information Figure S1),[15-17] this kind of Li nanorods can be fully detected by ^7Li NMR as the RF skin depth is about 12 μm (see supporting information). Therefore, a linear increase of the signal intensity during charge process is observed at low charge current of 0.1 mA for the cell with Cs^+ . However, only little fluctuations of intensities accompanied with following discharge and recharge process for both cells. In the

symmetric Li metal electrode cells, during charge/discharge process, both the stripped Li from cathode and the deposited Li on anode are detectable, no net increase of signal unless new detectable microstructures are formed.

When the cycling current is increased to 0.25 mA, the signal intensities of both cells increase linearly during initial charging process. While for the cell with Cs^+ , a linear decrease is also observed during discharge process (Figure 3b'). In fact, during discharge process, Li is stripped from the anode, so part of the microstructures is consumed, as some of the stripped Li are smoothly deposited on cathode except some deposited on the cathode to form new microstructures. There is a "V" turn between the 1st discharge and 2nd charge for the cell with Cs^+ , while for the cell without Cs^+ a typical "U" turn exists (Figure 3b). The differences between the peak point of the 1st charge and the lowest point of 1st discharge in the normalized intensity curves reflect the amount of deposited Li microstructures that can be eliminated on the electrode during discharge process. For the cell with Cs^+ it is 0.34, while for that without Cs^+ is only 0.18. This result indicates that the addition of Cs^+ can increase the self-cleaning capability of the electrode during cycling processes, in consistent with the SEM observation that the Li is stripped from the nanorods during the stripping process.[17] When the current is increased to 0.5 mA, the total amount of newly formed microstructures is much more significant, which indicates that more irreversible or dead Li structure formed at high current density no matter whether Cs^+ was added. This is consistent with our recent finding that the effect of Cs^+ on the protection of Li metal anode is reduced when the charge current density is increased.[28]

Moreover, the NMR results in Figure 3 indicate that more Li microstructures are formed for the cell with Cs^+ additive. Since the charge-discharge current used are the same for both the batteries with and without Cs^+ additive, more reversibility in NMR signal means that higher

Coulombic efficiency for Li deposition with Cs^+ additive. In contrast, less reversible NMR signal means more Li has been converted “dead” Li and does not participate in the following electrochemical processes. It can be inferred that the deposited micro-structured Li-metal may be evenly spaced for the cell with Cs^+ additive, and thus demonstrates better NMR receptivity. This picture is consistent with the finding from the *ex situ* SEM analysis of the Cu electrode in the Li|Cu|Li three-electrode cells, where evenly spaced nano-sized Li-fibers with even front tips spaced by SEI layers in between the fiber spaces were observed in the cell with Cs^+ additive.[17] In contrast, for the cell without Cs^+ additives, larger sized and irregular shaped Li-metal particles and thick fibers were observed. Our NMR results on the Li|Li batteries clearly support the findings reported previously. For larger sized Li-metal particles, due to the skin effect only a part of the Li-metal on the particle surface is observed by NMR. The poorer reversibility for battery without Cs^+ additive indicates that more Li is dead or electrochemical inactive, suggesting that some of the nano-structured Li is detached from the conducting Li-metal electrodes.

Though quantitative information of microstructures can be directly obtained by ^7Li NMR, the most concerned morphology information such as Li dendrite/nanorod deposited near the electrode can't be so directly distinguished. In order to gain further insight into the orientation details on Li microstructures deposited on the Li-electrode surface, the selected ^7Li spectra at a charge time of 10 h at 0.1 and 0.25 mA were de-convoluted by a series of orientation dependent peaks. Given the fact that the linewidth of the ^7Li signal for bulk surface of Li metal is fairly constant on the surface orientation of a single piece of flat Li-metal foil with respect to the external magnetic field $\mathbf{B}_0$ (i.e., about 600-800 Hz, see Figure S2) and the simulated main surface signal for Li-metal battery is about 1019 Hz, the most reasonable way to simulate the deposited Li dendrite/nanorod signal would be to use a group of peaks with half linewidth locked to around

1000 Hz. It is found that a minimum five peaks are needed to generate a good fit for the dendrite/nanorod signals from both the Li-metal cells without and with Cs^+ additives. The chemical shifts and the linewidths for both the deposited Li and the electrode Li, and relative distribution of deposited Li as a function of the normal direction of the Li-metal surface are summarized in Figure 4 and Table 1. For both cells with and without Cs^+ additive, the chemical shifts are similar, i.e., at about 260, 266, 270, 275 ppm, respectively, corresponding to the orientation of Li-metal surface (normal direction) to $\mathbf{B}_0$ of, 130° , 120° , 100° , and 90° respectively. Note that the Li-metal electrode signal is located at 252 to 247 ppm, corresponding to the surface (normal direction) of Li-metal electrode of 20 to 30° away from $\mathbf{B}_0$. Thus, the peaks at 266 to 271 ppm corresponding to deposited Li oriented nearly perpendicular to the Li-metal electrode surface. For the cell with Cs^+ the ratio of this part changes from 55% to 69%, while for the cell without Cs^+ it changes from 44% to 67% for charge at 0.1 mA and 0.25 mA. The percentage of perpendicularly deposited Li in the cell with Cs^+ is about 10% higher than that without Cs^+ at lower charge current at 0.1 mA, indicating more percentage of micro-structured Li is oriented perpendicular to the electrode surface in the case of battery with Cs^+ additive.

To get more insight information on Li deposition behavior in cells with and without Cs^+ , the signals of metallic Li (240-280 ppm) were separated into two major parts with respect to their overall orientations. The signal centered at or near 248 ppm is attributed to the metallic Li parallel to the electrode (Li-electrode) containing more information related to the plate surface of the electrode, while the signal centered at or near 266-267 ppm signal results from the metallic Li microstructures (Li-dendrite/nanorods) vertically deposited to the electrode, which contains more information related to the dendrite/nanorods.[25, 26] Thus, metallic Li migration between electrode surface and dendrite/nanorods can be quantitatively obtained.

The normalized signal intensities (see supporting information for details) of Li-electrode (I_{N-E}) and vertically deposited Li-nanorods (I_{N-D}) during cycling process are shown in Figure 5. The signal change trend of vertically deposited Li looks similar to that in Figure 3, where the total Li-metal signal was used, while the signal from the electrode Li shows an opposite trend. During the charge process Li is stripped from the cathode and deposited on the anode. If Li smoothly deposits onto the anode surface and forms an integrated part of the bulk Li-metal anode surface, the signal from Li-metal cathode should be constant for a symmetric Li-metal cell due to the unchanged skin effect. The results from Figures 5 clearly show that the signal from bulk Li-electrode decrease during the charge processes at various charge currents of 0.1, 0.25 and 0.5 mA. The decrease of the signal from bulk Li-electrode can be explained as follows. When RF penetrates the metal surface, its energy decreases exponentially to the depth (see the supporting information for details). Thus, the increase of vertically deposited Li nanostructures (either randomly oriented or aligned nanostructures) on electrode should have a screen effect on the part of electrode covered by them, which makes the effective power of RF received by this part decrease. Therefore, during charge process more and more vertically deposited Li is formed on the anode, which results in the signal decrease of the bulk Li electrode. During the discharge process the previously deposited Li in nanostructure and electrode Li is stripped from anode to form new dendrites/nanorods plus Li-electrode on the cathode side and the net amount of dendrite/nanorods decreases. Thus the screen effect is mitigated, which results in the signal increase from electrode Li.

When cycling at 0.25 mA (Figure 5b and 5b'), the batteries with and without Cs^+ both show the same trend during charge process. However, for the battery without Cs^+ , a short-time signal decrease of vertically deposited Li and simultaneous increase of electrode Li exists at the initial

stage of discharge process, then the decrease or increase trends become unobvious, and even over the second charge process the signal increase is still not obvious. In contrast, for the battery with Cs^+ , the linear decrease and increase trends maintain all the time. In fact, there are two ways of Li transportation that result in the signal changes during cycling process for the symmetric cell: 1) bulk Li electrode transfers to the nano-structured Li on the other electrode; 2) nano-structured Li transfer to the nanos-structured Li on the other electrode. An increasing NMR signal come from Li perpendicular to Li electrode means an increasing in aligned Li nanostructures. A decreasing NMR signal from Li parallel to Li electrode is related to decreased flatness of Li electrode. A stable NMR signal from Li parallel to Li electrode indicates that the structure is stable and cannot be reversed. It can be concluded that different change trends for cells with and without Cs^+ are results from the amount of Li participating in Li transfer between nano-structured Li and bulk Li metal electrode. For the cell with Cs^+ , more Li participate in the transfer between aligned nanorods and electrode. While for the battery without Cs^+ , Li transfer mainly occurs between the randomly aligned Li on different electrodes.

To investigate the role of Cs^+ additive, *in situ* ^{133}Cs NMR was carried out during the battery cycling at 0.1 mA by including extra amount electrolyte into the battery in order to emphasize the ^{133}Cs NMR signal from the liquid phase electrolytes. The results, shown in Figure 6 and Supporting Information Figure S5, clearly indicate that Cs^+ is migrated from the electrolytes of $\text{CsPF}_6\text{-PC}$ to the Li-metal surface, resulting in a continuous decrease of the Cs^+ in the electrolyte. This observation is based on the principle that the Cs^+ in the liquid state of the $\text{CsPF}_6\text{-PC}$ electrolyte has a narrow linewidth and is observed by *in situ* ^{133}Cs NMR. However, when Cs^+ is adsorbed onto the Li-metal surface, the linewidth becomes too broader to be observed by *in situ* NMR given the signal to noise obtained. The process of the Cs^+ adsorption onto the Li-metal

surface is at the very beginning of the charge cycle and lasts up to the point the first charge plateau is reached (see Figure 6 for details) and then an equilibrium is reached. The maintenance of the Cs^+ intensity also confirms the Cs^+ is not consumed during cycling process. This equilibrium is maintained afterwards and is independent of the charge-discharge cycles proceeding. One obvious explanation is that for the symmetric Li-metal battery, the Cs^+ adsorption on one electrode and desorption at the other electrode at the same rate due to the switch of polarity of the potential of two Li electrodes, which means Cs^+ adsorption-desorption is completely reversible. The results confirm that Cs^+ adsorbs on the anode forming positively charged electrostatic shield during charge process.[15]

Based on the above results and analysis, two growth models of Li deposition pattern are proposed in Figure 7. For the cell with Cs^+ (Figure 7a), during charge process, the growth of nanorods is restricted to a certain length and morphology as they are surrounded by positively charged electrostatic shield, which should prevent them from further growth when they reach the critical point.[15] Therefore, the morphologies of the Li nanorods should be uniform exhibiting as a smooth film. During the following discharge process, the nanorod-structured Li is stripped from anode, and at the same time the positively charged electrostatic shield is formed on the surface of nanorods on cathode, which force part of the stripped Li to be deposited on the adjacent regions of the electrode, which is indicated by a linear decrease of the signal of nanorods and a linear increase of the electrode signal due to the screen effect. This process repeats during the following cycles. However, for the cell without Cs^+ (Figure 7b), the growth of micro-structured Li (dendrite) is less homogeneous and more randomly orientated with some of them growing uneven length, thin and thicker rods and even detached from the electrode surface during the charge process. The thicker rods exhibit stronger screen effect on the electrode due to

the increased skin effect. During the following discharge process, Li is stripped from these dendrites, but initially the dendrites, which are thin and short, disappear first,[29] and only a small part of them deposited on the other electrode. Therefore, a short time decrease of the signal of vertically deposited Li and increase of electrode exists during the initial discharge process. With discharge proceeding, the growth of dendrite accelerates,[7] and almost all the stripped dendritic Li is deposited on the newly formed dendrite due to no restrictions. Li transportation between the dendrites of different electrodes is dominant, so there is no significant net amount change of dendrites. Thus, the signals remain to be unchanged. Even during the second charge process, this trend continues to nearly the end, and then a few new dendrites were formed, which is indicated by the signal increase near the end of the second charge. Though Li transportation between the electrodes is unavoidable during these processes, Li transfer between dendrites/nanorods is ready to occur as the electric field near the tip of dendrite/nanorod is much stronger, which should accelerate stripping and deposition rate of Li.

In fact, the addition of Cs^+ does not prohibit the vertically deposited porous Li, but it can effectively control the Li deposition behavior, where the deposited Li is uniform and ready to be stripped via transferring Li to the electrode. This kind of Li is electrochemically “active” during the cycling process, thus the electrodes show much better reversibility. While for the cell without Cs^+ , the dendritic growth is random and not restrained, and Li transport between randomly aligned nanostructures may finally result in the growth of some long and thick dendrites. Some isolated and “dead” Li is formed under this condition, which largely reduce the reversibility of the electrode.

Conclusions

A detailed *in situ* ^7Li and ^{133}Cs NMR investigation on the role of Cs^+ in Li deposition behavior was carried out in this work. Addition of Cs^+ significantly enhances the uniform Li deposition and the reversibility of the Li electrode during charge/discharge cycling process. The normalized total signal intensities of metallic Li demonstrate that the battery with Cs^+ shows a “V” turn while that without Cs^+ shows a “U” turn between the first and second cycles. Further detailed analysis was carried out by separating the signals from vertically deposited Li and the signal from the surface parallel to the bulk electrode Li. It is found that more vertically deposited porous nanofiber/nanorod Li was observed with Cs^+ additive compared to that without Cs^+ additive. The formation of Li microstructures has RF screen effect on the Li signal observed from the flat electrode surface. *In situ* ^{133}Cs NMR confirms the migration of Cs^+ from the electrolyte to the electrodes forming positively charged electrostatic shield near electrode during cycling process. Combining the screen effect and positively charged electrostatic shield formed by Cs^+ during cycling process, different Li deposition models are proposed for cells with and without Cs^+ during cycling process. More “active” porous and thin nanorods Li are formed and participating in Li transfer with electrode in the battery with Cs^+ , while some isolated or “dead”, including thick and dendritic Li is formed for the battery without Cs^+ . As a result, the batteries with Cs^+ additive show better reversibility during cycling process.

Acknowledgments

This work was supported by the Joint Center for Energy Storage Research (JCESR), an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences (BES). The NMR studies were conducted in the William R. Wiley Environmental Molecular Sciences Laboratory (EMSL), a national scientific user facility sponsored by DOE’s

Office of Biological and Environmental Research (BER) and located at PNNL. PNNL is operated by Battelle for the Department of Energy under Contract DE-AC05-76RLO1830.

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Table 1. The parameters extracted from the fitting of the spectra in Figure 4

		Deposited Li				Li electrode	
With Cs ⁺	δ (ppm)	260	266	271	275	248	252
additive	Orientation	(130°/110°)	(120°/100°)	(100°/80°)	(90°/70°)	(20°)	(30°)
	(B ₀ */electrode**)						
0.1 mA	$\Delta\nu_{1/2}$ (Hz)	1003	1003	1003	1003	700	1002
	(%)	36	36	19	9		
0.25 mA	$\Delta\nu_{1/2}$ (Hz)	1107	1165	1002	1002	874	1002
	(%)	29	52	17	2		
Without	δ (ppm)	259	266	270	276	247	252
Cs ⁺	Orientation	(130°/113°)	(120°/103°)	(105°/88°)	(90°/73°)	(17°)	(30°)
additive	(B ₀ */electrode**)						
0.1 mA	$\Delta\nu_{1/2}$ (Hz)	1002	991	1014	1165	652	1002
	(%)	32	14	30	24		
0.25 mA	$\Delta\nu_{1/2}$ (Hz)	991	1049	1049	1398	816	991
	%	13	37	30	20		

* Represent the angle between B₀ and normal direction of deposited Li metal surface;

** Represent the angle between deposited Li metal surface and Li electrode.

Figure Captions

Figure 1. Schematic diagram of *in situ* NMR cell setup.

Figure 2. Selected ^7Li NMR spectra (III and IV) for batteries without and with Cs^+ under cycling process (I and II are representative cycling curves and the detailed cycling curves at each current are shown in Figure3): a and a' pristine cell, b and b' charged at 0.1 mA, c and c' discharged at 0.1 mA, d and d' second charged at 0.1 mA, e and e' before charge at 0.25 mA, f and f' charged at 0.25 mA, g and g' discharged at 0.25 mA, h and h' second charged at 0.25 mA, i and i' before charge at 0.5 mA, j and j' charged at 0.5 mA, k and k' discharged at 0.5 mA, l and l' second charged at 0.5 mA. (The *in situ* experiments were carried out sequentially from 0.1 mA to 0.5 mA.).

Figure 3. Normalized total signal intensities ($I_{\text{N-sum}}(n)$) of metallic Li and corresponding potential curves for batteries without (top) and with Cs^+ (bottom) under different cycling currents: a and a' 0.1 mA, b and b' 0.25 mA, c and c' 0.5 mA.

Figure 4. Selected *in situ* ^7Li NMR spectra for batteries without Cs^+ charged at 0.1 mA (a) and 0.25 mA (b) for 10 h, and with Cs^+ charged at 0.1 mA (c) and 0.25mA (d) for 10 h. Dashed lines represent the simulated peaks. Black and red lines represent the experiment and simulated spectra, respectively.

Figure 5. Normalized signal intensities of Li-electrode ($I_{\text{N-E}}$), vertically deposited Li ($I_{\text{N-D}}$) and corresponding potential curves for batteries without and with Cs^+ under different cycling currents: a and a' 0.1 mA, b and b' 0.25 mA, c and c' 0.5 mA.

Figure 6. Normalized signal intensities of Cs^+ for the cell with Cs^+ during cycling process. Note that two pieces of glass fiber separators and extra amount of electrolytes were included in between the two symmetric Li-electrodes to enhance the ^{133}Cs NMR signal.

Figure 7. Lithium deposition models of batteries: with (a) and without (b) Cs^+ additives.

Figures

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7