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# A salt-derived solid electrolyte interphase by electroreduction of water-in-salt electrolyte for uniform lithium deposition

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- he concept of salt-derived solid electrolyte interphase is proposed
- his lm is rich in inorganic components mainly i $_x$ $_y$ and i
- his lm greatly reduces the overpotential and facilitates fast $i^+$ transport
- igh oulombic ef ciency and uniform spherical i deposition are achieved
- his wor emphasi es the functions of salt decompositions on protection of i

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Water-in-salt
olid electrolyte interphase
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lectroreduction
pace charge

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otorious growth of dendritic lithium with low oulombic ef ciency causes safety and stability issues, which hinder practical applications o control the lithium deposition so that one has a dendrite-free lithium metal anode with high oulombic ef ciency is highly desirable but challenging ere, this wor reports a copper substrate covered by a salt-derived solid electrolyte interphase that produced by electroreduction of a highly concentrated water-in-salt electrolyte to reali e stable lithium deposition uite distinct from the resistive layer comprised principally of solvent-derived organic species such as lithium al yl carbonates that produced in conventional dilute electrolyte, this salt-derived solid electrolyte interphase is rich in inorganic components mainly i $_x$ $_y$ and i , which effectively reduce the overpotential and facilitate fast $i^+$ transport n addition, a small number of reduced uorine organic anions - $_x$ stabili e the space charge to give a uniform distribution of $i^+$ uch a solid electrolyte interphase on the copper substrate is able to modulate the lithium plating stripping to produce uniform spherical lithium deposition with no dendrites, and a high oulombic ef ciency $\approx$ is achieved his wor provides a uni ue strategy to enlarge the functions of the lithium salt decompositions on the protection of lithium metal anodes

## 1. Introduction

ithium-ion batteries s have achieved great success for use in portable devices and electric vehicles, but are unable to meet the currently ever-increasing demands of energy density 1 he fact that the i metal, with a speci c capacity of an order of magnitude greater than that of the state-of-the-art i anode, has attracted great interest in achieving rechargeable batteries with a higher energy density , owever, there is still a long way to go before the practical application of i metal due to its poor safety, low oulombic ef ciency and short lifespan, its parasitic reactions with li uid electrolytes, and unstable and uncontrollable dendritic electrodeposition

uch unsolved issues are associated with the high activity of i metal i metal, which has the most negative electrochemical potential

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– vs a standard hydrogen electrode , can react spontaneously with all polar aprotic solvents , When fresh i metal is exposed to the electrolyte, an electrically insulating but ionically conducting solid electrolyte interphase lm is

interfacial electrochemical process on the electrode surface ecently, the emerged concept of water-in-salt electrolyte has been used to expand the electrochemical window of s At room temperature, the maximum solubility of universal i salt in water is about 1 At concentrations of i above , the reduction potential of $^{-}$ is altered by its interaction with $i^{+}$ Aggregates such as i $_{x}$ become unstable below vs $i^{+}$ i , which is higher than the reduction potentials of 1 for isolated $^{-}$ and for hydrogen both vs $i^{+}$ i n such an electrolyte, a dense lm dominated with i is formed as a result of reduction of the $^{-}$ by the $i^{+}$ solvation sheath, which prevents further sub-reactions

sing this concept, we reported an electroreduction route to construct an arti cial inorganic-rich lm derived from reduced salt anions on u substrate ig 1 n a typical three-electrode cell ig 1 , a u foil as the wor ing electrode was immersed in the water-in-salt electrolyte, and cyclic voltammetry scans were then performed in the range 1 – vs $i^{+}$ i with a scan rate of 1 m $s^{-1}$ for 1 cycles the experimental details are available in aterials and methods

After pre-processing, the at u foil was covered by a dense interphase with a large number of nanoparticles ig a and b ore importantly, the cross-view image of the u with the lm showed that a thin lm composed of nanoparticles covered on u surface igs b–c , which were composed of , and elements igs d–f A transmission electron microscopy image clearly showed that the u substrate was decorated by nanoparticles of few to tens of nanometers si e ig c and ig igh-resolution images of the lm showed the crystal lattice of the nanoparticles, corresponding to inorganic products i and i ig d nergy-dispersive -ray spectroscopy analysis also demonstrated that , , and were evenly distributed on the u substrate ig e–i o probe the chemical composition of the lm on the u substrate, -ray photoelectron spectroscopy was carried out he surface of bare u using i u half cells in 1 i i electrolytes after cycles was also characteri ed by he strong signal detected in the 1s spectrum between and e can be assigned to i or - $_{x}$ species ig a he p spectrum pea s detected at 1 , 1 , 1 and 1 e corresponded to i , i , i and – ig b , respectively – he inorganic species i $_{x\ y}$ i , i and i accounts for but 1 for the organic species according to the pea area n contrast, the solvent-derived solid electrolyte interphase on bare u is principally composed of organic – species almost 1 or the 1s spectrum ig c , inorganic species i , i and i in accounts for based on the pea area ig c he detected signals of were mainly from two species a few uorine organic anions - $_{x}$ at ≈ e originating from partially reduced fragments, and dominant i at ≈ e ig d , he proportion of i in the lm accounts more than the solvent-derived lm on bare u 1 based on the ratio of pea area ere, , , and are considered as the main species in the lm and normali ation processing is carried out As the able 1 shows, the ratio of inorganic species in the salt-derived lm 1 , atomic ratio is far greater than that in the solvent-derived lm , atomic ratio herefore, we conclude that the lm is rich in inorganic components mainly i $_{x\ y}$ and i than the solvent-derived lm As previous reports, on one hand, i is a good electrical insulator ≈1 $^{-1}$ $cm^{-1}$ to prevent electrons from crossing the lm n the other hand, i has been demonstrated to greatly suppress dendritic i growth due to its high surface diffusivity for $i^{+}$ one of the inorganic products was a decomposition product of residual salts caused by -ray radiation ig herefore, the lm is principally composed of inorganic i $_{x\ y}$ and i species, accompanied by a small amount of organic - $_{x}$ he chemical composition of the lm was also investigated using time-of- ight secondary ion mass spectrometry - in both negative and positive modes everal negative species were detected ig e , including $^{-}$ $m/e=1$ , $^{-}$ $m/e=$ , $^{-}$ $m/e=1$ and $^{-}$ $m/e=1$ n particular, the signal from $^{-}$ species was much stronger than from other species, which illustrated the high content of uoride in the lm he positive mode of - was also measured under the same conditions and a positive cluster specie i $^{+}$ $m/e=$ was observed ig f o estimate the thic ness of the lm, we conducted 1 s $s^{+}$ sputtering to obtain a depth pro le ig As the sputtering time increased, the signal of the detected species all went down iven that and represented the components of the lm, their declining trend suggested that the average thic ness of the lm was ≈1 nm t = 1 s and sputtering rate = nm $s^{-1}$

he electrochemical pre-processing was performed under air atmosphere o exclude the interference of gases li e , we performed control experiments under an Ar atmosphere imilar to the results under air, a series of inorganic products, such as i , i , i , i , i $_{x\ y}$, were generated ig , the main difference being the absence of i under Ar atmosphere urface-enhanced aman spectra for the lm also con rmed that the i generated was associated with ig eanwhile, active species in aman spectra, such as i centered near $cm^{-1}$ and i at 1 $cm^{-1}$ were detected his result is consistent with the results etailed analyses are given in the upporting nformation

ombining the above results and analyses, the lm on the u substrate was generated by the electrochemical pre-processing and consisted of reductive decomposition products of the $^{-}$ Whether annealed under Ar or air atmospheres, the main reduced products of i are i and i $_{x\ y}$, accompanied by a small amount of - $_{x}$ he formation mechanisms of the lm are as follows

$$LiN(SO_2CF_3)_2 + ne^- + nLi^+ \rightarrow LiF + Li_3N + Li_2S_2O_4 + Li_{n\text{-}5}C_2F_5 \quad 1$$

$$LiN(SO_2CF_3)_2 + e^- + Li^+ \rightarrow LiNSO_2CF_3 + LiSO_2CF_3$$

$$Li_2S_2O_4 + 4e^- + 4Li^+ \rightarrow Li_2SO_3 + Li_2S + Li_2O$$

$$Li_2O + CO_2 \rightarrow Li_2CO_3$$

he lm obtained by electrochemical processing is distinct from the conventional lm formed in a nona ueous electrolyte ig 1 he conventional passivated lm is principally composed of solvent-derived organic species li e i $i^{+}$ move sluggishly through the organic species by pore diffusion, which produces a low ionic conductivity and an uneven charge distribution he non-uniform $i^{+}$ ux and local high concentrations of $i^{+}$ accelerate the growth of i dendrites and consumption of the electrolyte ather than a highly resistive layer, this new lm is largely inorganic mainly i $_{x\ y}$ and i with a small number of uorine organic anions - $_{x}$ i $_{x\ y}$,


**Fig. 1.** chematics of the i plating behavior on different substrates

provide superior ionic conductivity and fast $i^+$ diffusion , he abundance of i , with a high surface energy, produces a small interfacial resistance and uniform spatial distribution of $i^+$, also suppressing dendritic i growth n addition, the - $_x$ species inhibit space charge accumulation, which induces a homogeneous $i^+$ distribution and facilitates homogeneous i deposition 1, As the plating process proceeds, the lm facilitates the fast and uniform deposition of spherical i particles, resulting in a stable cycling performance

he i plating behavior on the u substrate with the lm was evaluated in a coin cell bare u substrate was the controlled

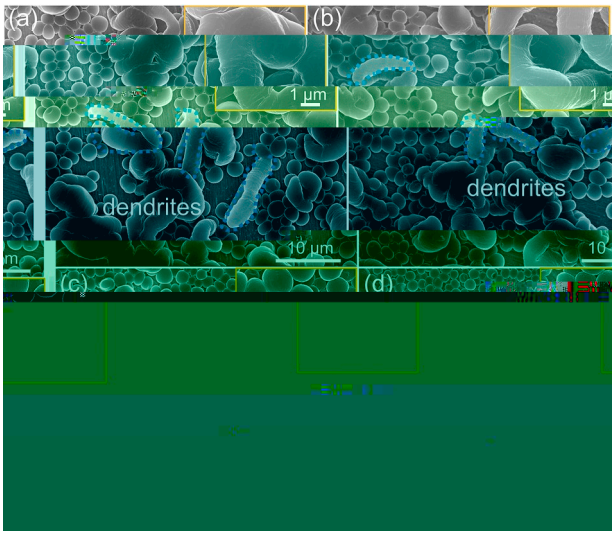


**Fig. 4.** orphologies of the 1st i nuclei on bare u substrate and the u substrate with lm images of i nuclei on the bare u substrate at a 1 and b mA cm⁻ images of i nuclei on the u substrate with the lm at c 1 and d mA cm⁻ he insets are high-magni cation images of the i nuclei

rised to a relatively stable voltage plateau at – m vs $i^+$ i , which was the mass-transfer-controlled overpotential he nucleation overpotential is de ned as the difference between the minimum voltage and the later stable mass-transfer-controlled overpotential , which was 1 m for a bare u substrate n contrast, the curve of the u substrate with the lm had a much smaller voltage minimum of – m vs $i^+$ i at the nucleation stage, with a nucleation overpotential of only m he mass-transfer overpotential depends on the applied current density and the migration properties of the $i^+$ At the same current density of mA cm⁻ , the u substrate with the lm had a smaller mass-transfer overpotential of m compared to m for bare u he lower mass-transfer controlled overpotential indicated that the lm effectively improved i electrodeposition inetics lectrochemical impedance spectroscopy analysis of the cells was conducted to illustrate the inetic behavior of the anodes ig b oth y uist plots had a semicircle in high fre uency region, which was ascribed to $i^+$ migration through the lm on the electrode surface f the average thic ness of lm is about 1 nm ig , a high $i^+$ conductivity × 1 ⁻ cm$^{-1}$ is achieved by the lm, around two times higher than bare u 1 × 1 ⁻ cm$^{-1}$ he good conductivity of $i^+$ migration through the lm con rmes a fast $i^+$ transport inetics

o further investigate the reliability of the u substrate with the lm, the of i plating stripping was analy ed in i u cells with 1 mA h cm⁻ of pre-deposited i he cut-off voltage of recharge was xed at 1 vs $i^+$ i he electrochemical performance of different thic ness of lms on u substrate was evaluated ig As the increasing number of pretreatment, the thic ness of the lm nally reach to a maximum ≈1 nm when the lm is too thic to transport electrons ig f n accordance with the thic ness of the lm, the initial was increased from to higher than the bare u he for the u substrate with the lm 1 nm uic ly increased to after several cycles and remained stable for 1 cycles ig c he high can be attributed to the lm which effectively reduces side reactions between the deposited i and the electrolyte After increasing the current density to 1 mA cm⁻ ig a , the initial of the u substrate with the lm exhibited 1 , which exceeded the u substrate And then the increased to a high average over 1 cycles without failure ven at a high current density of mA cm⁻ ig b , the i plating stripping was stable without uctuation owever, cells with the bare u substrate showed a rapid loss of performance after cycles at mA cm⁻ and cycles at 1 mA cm⁻ o observe the i deposition morphologies, we disassembled the i u cells after cycles A large number of i dendrites with sharp tips had formed at different current densities ig d and ig or irregular and random i growth, increased contact area with the nona ueous electrolyte further consumed active i metal and electrolyte, producing a low As a comparison, the plated i with lm became larger and thic er while maintaining the spherical morphology of the i even after plating stripping cycles ig e and ig 1 hese different results con rm that the lm produces uniform i deposition without i dendrites

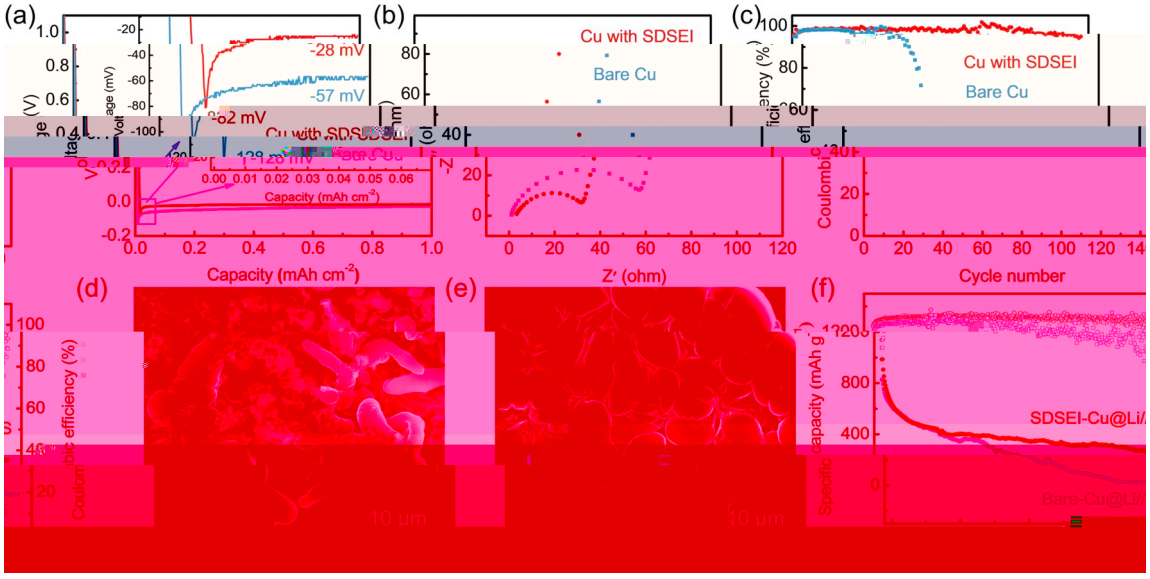


**Fig. 5.** lectrochemical performance of i u cells a oltage-time curves after the 1st i nucleation at mA cm⁻ b of i u cells after the 1st cycle c of i deposited on bare u substrate and the u substrate with the lm at mA cm⁻ he cells were tested with a xed areal capacity of 1 mA h cm⁻ d image of the i morphology on the bare u substrate and e the u substrate with the lm f lectrochemical performance of - u i and are- u i cells

i– full cells were assembled to verify the advantages of the above strategy for practical use with mA h cm⁻ of pre-deposited i i– cells based on the u substrate with the lm and the bare u substrate are denoted - u i and are- u i , respectively he are- u i cell exhibited a about 1 in the rst cycles ig f owever, beyond cycles, it uic ly dropped to , accompanied by a fast