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25 **Abstract:**

26 Long-term stability of reference electrode is a major issue in lithium-ion batteries. A composite
27 Ni-Li reference electrode (RE) with a longer lifetime than traditional Cu-wire Li reference
28 electrodes is proposed in this study. However, the larger size of the Ni-Li RE creates a blocking
29 effect when positioned internally in the battery. The blocking effect manifests as an abnormal
30 feature in the measured electrode potential. A two-dimensional (2D) finite element model of the
31 cell with an internal RE is constructed to investigate the mechanism of the blocking effect. The
32 internal RE blocks the path of local current flow in the electrolyte, and decreases the
33 electrochemical reaction rate of particles in the anode and cathode, leading to measurement errors.
34 Characteristic lengths of RE and applied currents were examined as parameters in the finite
35 element model to determine their effect on the magnitude of error. A useful guide is provided for
36 proper selection of size of RE and applied current in dynamic tests of lithium-ion batteries.
37

38 1. Introduction

39 Lithium-ion batteries are widely used in consumer electronics, electric vehicles, and energy
40 storage, because of their high energy and power density^{1, 2}. A RE is important in carrying out
41 experimental tests and mechanistic investigations of lithium-ion batteries³⁻⁹. Electrode properties
42 such as impedance or potential can be ascertained from information provided by a RE. This
43 information enables some aging mechanisms and safety issues, such as solid electrolyte interphase
44 (SEI) growth and such as internal short circuit¹⁰ caused by lithium deposition, to be identified.
45 Although present commercial lithium-ion batteries do not have REs, most battery manufacturers
46 are interested in monitoring the state of lithium plating with the help of a RE to improve battery
47 safety and performance. Thus, there is a need for REs in battery research and industrial
48 production.

49 Three categories of RE materials are used in lithium-ion batteries. The first, and most common, is
50 lithium metal^{4, 5, 7-9, 11-13}, which is intrinsically compatible with the non-aqueous electrolyte of the
51 battery, provides a stable value against which the electrode potential is measured. Although the
52 electrode potential of lithium metal is -3.04 V vs. the standard hydrogen electrode (SHE), it is
53 customary to report potentials versus the Li/Li⁺ value. This is convenient for post-processing
54 experimental data. Lithium metal is also readily and reproducibly produced. The second class of
55 RE materials includes lithium compounds, such as LiFePO₄ (3.4 V vs. Li/Li⁺) and Li₄Ti₅O₁₂ (1.5
56 V vs. Li/Li⁺) etc.¹⁴, which have a known potential plateau. Lithium-containing RE must be
57 oxidized to a specific state of charge (SOC) to provide a stable equilibrium potential. The third
58 category of materials comprises binary lithium alloys, the most common of which is the Li-Sn
59 alloy.^{3, 15, 16} Li-Al¹⁷, Li-Au¹⁸, and Li-Bi⁶ alloys also have been recommended as RE materials for

60 impedance and potential measurements. Lithium-alloy materials require a lithiation pretreatment
61 to produce a stable reference potential. Because the lithium alloys typically exhibit more than one
62 potential plateau, the process must be conducted carefully to produce the desired reference
63 potential. A disadvantage of lithium compounds and alloys is reference potential drift due to
64 lithium loss from the electrode. For this reason, we focus on lithium-metal RE materials.

65 Although REs are commonly used in potential and impedance measurements in lithium-ion
66 batteries, some unsolved problems remain. For example, experimental distortions and artifacts are
67 frequently observed. Jansen et al. investigated the effects of the RE size and placement and cell
68 geometry on impedance measurements¹⁹. They concluded that a large internal RE can adversely
69 affect impedance measurements and the misalignment of an external RE can cause errors in
70 impedance measurements. Ender et al. evaluated the effects of geometric and electrical
71 asymmetries using an external RE and found distortions in scaling factors and inductive artifacts
72 in the impedance response²⁰. Klink et al. demonstrated that geometrical asymmetry can be reduced
73 by precise electrode alignment and use of a coaxial RE.²¹ Delacourt et al. proposed a novel
74 three-electrode cell set-up, in which, holes in the working and counter electrodes for RE
75 positioning minimized distortions in the impedance spectrum.²² Hoshi et al. suggested that the RE
76 should be positioned externally between the positive and negative electrodes for optimum EIS
77 measurements.²³ Ender et al. examined point-like, wire, and mesh RE designs and demonstrated
78 theoretically and experimentally that a mesh RE best achieves distortion-free EIS measurements.^{8,}
79 ²⁴ Although EIS measurements with a RE have been investigated extensively, only a few studies
80 have examined the effects of RE placement and design in dynamic tests of lithium-ion batteries,
81 which are important in investigating the fast charge^{11, 25} and aging mechanism.^{4, 7, 26, 27} Klett et al.

82 compared positive and negative electrode potentials measured simultaneously with internal and
83 external REs during a 10 s, 3 C pulse charge, and found that the internal RE is more accurate.¹⁶
84 However, poor long-term stability of REs is a major issue, particularly in investigations of
85 capacity fade. Designs based on Li-plating onto a Cu wire exhibit potential drift shortly after
86 production, because the small amount of lithium is easily dissolved or consumed by SEI growth.
87 Lithium alloys, which exhibit multiple potential plateaus, presumably suffer from potential drift
88 when the intercalation state is unexpectedly altered.¹⁵ This also occurs with lithium compounds.
89 Therefore, lithium metal remains the most suitable RE material for lithium-ion batteries, despite
90 its possible depletion in the electrolyte.

91 In summary, an internal lithium RE, which provides more accurate electrode potential
92 measurement, is preferred for dynamic testing, although a small size is needed to reduce blocking
93 effects. However, the amount of active lithium must be as large as possible to extend electrode
94 lifetime. The trade-off between measurement accuracy and lifetime is a limiting factor in the
95 application of Cu-wire based lithium REs.

96 In this study, a new RE design with a greater active lithium loading is proposed and compared in
97 terms of performance with the Cu-wire-Li RE. The blocking effect of an internally positioned RE
98 also is investigated under dynamic conditions based on experimental measurements and a 2D
99 electrochemical model. Quantitative analysis of the blocking effect provides a general guide for
100 selecting the proper characteristic length of RE and range of applied current.

101 **2. Experiment and model description**

102 **2.1 Reference electrode setup**

103 Two reference electrode setups were compared to evaluate the effect of RE geometry on electrode

104 potential measurements in dynamic battery tests.

105 Lithium metal deposited onto a Cu wire substrate was used for Setup 1. The diameter of the Cu
106 wire was 25 μm , which approximates the dimension of the separator. One tip of a 2-cm-long Cu
107 wire was immersed in dilute sulfuric acid and washed thoroughly with stirring in water and
108 ethanol. This process produced a Cu wire with a polished tip ready for lithium deposit. The
109 polished tip was inserted carefully into the jelly roll between positive and negative electrodes. The
110 inserted portion of Cu wire was covered by a separator to avoid an internal short circuit. After
111 assembly, a 20- μA direct current was passed between the Cu wire and positive electrode and Cu
112 wire and negative electrode successively for 1 h to form a uniform lithium deposit.²⁸ This
113 completes production of the Cu-wire-Li RE.

114 Lithium metal applied to a Ni-foam substrate was used for Setup 2. The larger size of the Ni foam
115 (ca. 0.1-mm thick \times 1-mm wide) provided greater lithium loading. As described by Cui et al.²⁹ and
116 Zhang et al.³⁰, a piece of Ni foam was immersed into molten lithium, which formed a composite
117 RE by infusion of Li into the Ni host. One side of the RE was attached to a Ni current collector by
118 ultrasonic welding.

119 Subsequent experiments demonstrated that RE reliability and lifetime were greater with Setup 2.
120 Because lithium is consumed during use, a greater amount of lithium leads to a longer RE
121 lifetime^{6,28}. The superior performance of Setup 2 is attributed to its greater lithium loading, which
122 unavoidably introduces blocking effects due to RE size.

123 **2.2 Experiment**

124 Two commercial $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ (NCM)/graphite batteries with nominal capacities of 40 Ah
125 for Cell A and 24 Ah for Cell B were selected for experimentation. Set-up 1 was applied to Cell A

126 and Set-up 2 to Cell B. Setup 1 was applied to Cell A. Setup 2 was applied to Cell B. Cells A and
127 B were large enough to neglect the impact of the RE on the cell terminal voltage. However, there
128 was a difference in the time of RE emplacement. The Cu wire in Setup 1 was inserted into the
129 jelly roll before the cell was sealed with the help of the manufacturer. In Setup 2, Cell B was
130 discharged to 2.5 V and transferred to a dry room with a dewpoint of -70 °C. The Al-plastic film
131 of Cell B was carefully cut open and partially peeled away to leave enough space to separate the
132 positive and negative electrodes and insert the Li-Ni RE, which was wrapped with an additional
133 piece of separator to inhibit short-circuiting. The cell was resealed using a new Al-plastic film
134 with the Li-Ni RE positioned between the positive and negative electrodes.

135 It is worth mentioning that one-terminal and two-terminal configurations were typically used for
136 application of REs. Although there is no issue of inconsistency in the one-terminal configuration,
137 there is an undesirable interaction with the measuring circuit when the anode and cathode are
138 monitored simultaneously. The effect is suppressed in the two-terminal configuration, but either
139 format is feasible for electrode potential measurements. In this study, we adopt the one-terminal
140 configuration, because it is sufficient to investigate the blocking effect of the RE.

141 A series of dynamic tests were performed on Cells A and B after the REs were implanted to
142 examine the impact of RE size on electrode potential measurements.

143 1) Capacity test: Cells were charged with a constant current-constant voltage (CC-CV) protocol
144 until the upper cut-off voltage and cut-off current were reached. This was followed by a constant
145 current (CC) discharge to a lower cut-off voltage. A rest period was observed between charging
146 and discharging. Three cycles were conducted to evaluate the reproducibility of the voltage
147 measurement. The voltage ranges of Cells A and B were 4.2–2.8 V and 4.2–2.5 V, respectively.

148 The currents applied for charging and discharging, as suggested by the manufacturers, were 1 and
149 1/3 C for Cells A and B, respectively. The cut-off current was preset at 0.05 C for both cells.

150 2) C-rate test: Cells were charged at C-rates of 0.2, 0.5, and 1 C. The C-rates of discharge
151 suggested by the manufacturers were 1 and 1/3 C for Cells A and B, respectively. A 2 h rest period
152 was applied between charging and discharging to allow the cells to regain equilibrium.

153 3) RE test: This test was designed to compare different ranges of SOC operation. Two discharge
154 protocols with differently terminated SOC's were performed with Cell B. The cell was first
155 discharged at a rate of 1/3 C from 0.03 to 0 SOC followed by a 1h rest period. The cell was then
156 charged to 0.5 SOC at a rate of 1/2 C followed by a 3 h rest period. Finally, the cell was
157 discharged at a rate of 1/3 C from 0.5 to 0.2 SOC followed by a 3 h rest period.

158 All tests were performed on an 8-channel Neware BTS 4000 test station. The electrode potential
159 was measured with a 6 1/2-digit multimeter (Keithley 2000) with an input impedance of >10 GΩ.

160 The high input resistance reduces the leakage current to 100 pA or less, which improves
161 measurement accuracy and minimizes consumption of the reference electrode. The digital
162 multimeter was used in combination with a 10-channel scanner (Keithley 2000-SCAN), which
163 enabled simultaneous measurement of the anode and cathode potentials. The positive input of the
164 multimeter was connected to the current collector of the negative/positive electrode, and the
165 negative input was connected to the current collector of the reference electrode.

166 **2.3 Finite element model (FEM)**

167 A 2D FEM was built to investigate battery behavior with an internal RE. Fig. 1 shows the
168 schematic shows a schematic of the 2D FEM geometry for simulation. Characteristic widths and
169 thicknesses are considered in the model, which neglects the deformation of the separator and

170 electrode caused by implanting the RE.

171 The electrochemical model is configured to a 2D description of the cell dynamics. Apart from the
172 presence of the RE, the model is based on the work of J. Newman et al.³¹ Charge and mass
173 conservations are formulated by different partial differential equations (PDE) in the solid and
174 electrolyte phases with corresponding boundary and initial conditions and coupled with a kinetic
175 equation to describe the relationship between the overpotential and the lithium exchange flux (i.e.,
176 a Butler-Volmer equation). The principal equations are introduced here without their boundary and
177 initial conditions.

178 Mass conservation in solid phase is given by:

$$\frac{\partial c_s}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_s}{\partial r} \right) \quad (1)$$

179 where D_s is the solid phase diffusion coefficient. Mass conservation in the electrolyte phase is
180 given by:

$$\frac{\partial}{\partial t} \varepsilon_e^j c_e = \nabla \cdot (D_{e,\text{eff}}^j \nabla c_e) + a_s (1 - t_+) j, \quad j = \text{n,p} \quad (2)$$

$$\frac{\partial}{\partial t} \varepsilon_e^s c_e = \nabla \cdot (D_{e,\text{eff}}^s \nabla c_e) \quad (3)$$

181 where ε_e is the volume fraction of electrolyte, and $D_{e,\text{eff}}$ is the effective electrolyte diffusion
182 coefficient. Eq. (2) is used in the negative and positive electrode regions, while Eq. (3) is used in
183 the separator region. The lithium exchange flux, j , equals zero in the separator region. Charge
184 conservation in the solid phase is:

$$\nabla \cdot (\sigma_{\text{eff}} \nabla \phi_s) - a_s F j = 0 \quad (4)$$

185 where σ_{eff} is the effective electrical conductivity in the solid phase. Charge conservation in the
 186 electrolyte phase is:

$$\nabla(\kappa_{\text{eff}} \nabla \phi_e) + \nabla \left(\frac{2RT(t_+^0 - 1)\kappa_{\text{eff}}}{F} \left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_e} \right) \nabla \ln c_e \right) + a_s F j = 0 \quad (5)$$

187 where κ_{eff} is the effective electrical conductivity in the electrolyte phase. The kinetic equation has
 188 the form:

$$j = k_0 c_e^{1-\alpha} (c_{s,\text{max}} - c_{s,e})^{1-\alpha} c_{s,e}^{\alpha} \left(\exp\left(\frac{(1-\alpha)F}{RT} \eta\right) - \exp\left(\frac{-\alpha F}{RT} \eta\right) \right) \quad (6)$$

$$\eta = \phi_s - \phi_e - U_{\text{eq}} - FR_{\text{SEI}} j \quad (7)$$

189 where k_0 is reaction rate constant. The overpotential, η , is defined in Eq. (7), where U_{eq} is the
 190 equilibrium potential for the charge transfer reaction.

191 The rectangular RE is positioned between the two electrodes as shown in Fig. 2. Lithium
 192 exchange occurs only on the surface of the RE. Therefore, the charge conservation in the RE
 193 region is:

$$\nabla(\sigma^{\text{RE}} \nabla \phi_s) = 0 \quad (8)$$

194 where σ^{RE} denotes the electrical conductivity of the RE (lithium metal). The electrode potential
 195 measured versus the solid phase potential of the RE is given by:

$$\phi_s^{\text{RE}} = \phi_e + U_{\text{eq}}^{\text{RE}} \quad (9)$$

196 where the equilibrium of the RE is equals zero. This equation is applied on a presentative point on
 197 the surface of the RE and simulated electrode potential is equal to the difference between the solid
 198 potential of the electrode and the RE. All the simulations were carried out in Comsol
 199 Multiphysics.

200 **3. Results and Discussion**

201 **3.1 Abnormal feature(s) of the electrode potential**

202 To determine if overall battery performance is affected by the presence of an internal RE, cell
203 capacities were compared with and without the RE. For Setup A, the cell capacity of 40.39 Ah
204 without the RE changed to 39.89 Ah after the RE was implanted. For Setup B, the cell capacity
205 was 25.10 and 25.01 Ah before and after RE implantation, respectively. The internal RE appears to
206 have little impact on the battery performance. The anode potential in Setup A was always greater
207 than 0 V during the C-rate test, whereas the anode potential in Setup B decreased to 0 V at 0.5 and
208 1 C. The electrode potential profiles in Setup B also exhibited an abnormal feature compared with
209 Setup A. Fig. 3 illustrates the characteristics of the abnormal feature by comparing electrode
210 potential profiles for Setups A and B during rest periods in the C-rate tests. For Setup A, a
211 continuous decrease is observed in the cathode or anode potential during the rest period, which is
212 attributed to a depolarization. However, this behavior is not observed with Setup B. The at-rest
213 anode potential after cell discharge first decreases for ca. 1 h, but is followed immediately by a
214 curious increase. Similar behavior also occurs after a rapid initial decrease in the at-rest cathode
215 potential following cell charging. These observations contrast distinctly with the anticipated
216 depolarization behavior of an electrode according to the electrochemical battery model.

217 The abnormal change in voltage that appears reproducibly in the dynamic experiments is
218 considered to be a genuine feature rather than an experimental artifact. The presence of the feature
219 demonstrates that an internal RE produces pronounced differences in electrode potential behavior
220 during dynamic tests of lithium-ion batteries. Differences in the excitation time and time constant
221 are observed between the cathode and anode potential responses, which suggest that the feature is

222 governed by electrode architecture and material properties. The defining characteristic of the
223 abnormal feature is the anomalous increase in anode/cathode potential during the rest period
224 following cell discharge/charge rather than a continuous decrease until an equilibrium state is
225 reached. A schematic depiction that highlights the abnormal feature is presented in Fig. 4 (b) with
226 the abnormal increase highlighted. Fig. 4 (a), displays the normal response for comparison.

227 **3.2 Model fitting**

228 Specifically designed RE dynamic experiments were conducted to examine the origin,
229 characteristics, and mechanism of the abnormal feature. The anode potential was the first
230 parameter investigated. A short-term discharge was conducted to see if operation time was a factor.
231 Cell B was allowed to rest for 3 h to ensure full relaxation and then discharged as shown in Fig. 5
232 (a) with a current of $1/3$ C from an initial voltage of 3.265 V to a cut-off voltage of 2.500 V for
233 264 s followed by a rest period of 1 h. The anode potential in Fig. 5 (b) increases initially from
234 0.387 to 0.501 V until the end of discharge and then decreases to 0.473 V over the next 60 s
235 followed by an increase to 0.553 V at the end of the rest period. This confirms that the abnormal
236 feature is present even after a short period of operation.

237 A second experiment was conducted to examine the effect of the SOC on the abnormal feature,
238 because the cell had been discharged to 0 SOC in all previous experiments. Cell B was adjusted to
239 0.5 SOC by first discharging to 0 SOC and then recharging at 1 C for 30 min followed by a 3 h
240 rest period. The cell was then discharged from 0.5 to 0.2 SOC at $1/3$ C for 0.86 h followed by
241 another 3 h rest period as shown in Fig. 6. The anode potential increases from 0.147 to 0.219 V
242 during discharge and then decreases to 0.207 V over 380 s before reversing and increasing slightly
243 to 0.209 V during the rest period. The behavior of the abnormal feature is much less pronounced

244 in the second experiment, wherein the potential increment is 0.002 V rather than 0.080 V. This
245 difference may result from operation over different SOC ranges, which will be elaborated upon in
246 the next section.

247 **3.3 An explanation of the abnormal feature: blocking effect**

248 Very little discussion was found in the literature on the behavior we have observed, because
249 electrode potential data, which have been measured with different REs, have not been closely
250 examined during rest periods. The origin of the abnormal feature is explored in this section. There
251 are two likely sources of the difference in electrode potential behavior between Setup A and Setup
252 B.

253 The first possible cause is the RE itself, which suggests that its potential may deviate from the
254 standard value. In this case, undesirable reactions may occur at the interface between the Li metal
255 and electrolyte leading to SEI film formation. When the RE is immersed in the electrolyte,
256 parasitic reactions between metal and electrolyte species occur immediately and form compact,
257 insoluble products on the RE³². These reactions may alter the RE potential. However, the
258 behavior of Li as a RE differs from that as an anode. Very little current is applied to the RE,
259 because of the high input impedance of the voltmeter. Therefore, reactions between Li and the
260 electrolyte should be minimal. The difference in time constant between the anode and cathode
261 potential response indicates that the abnormal feature is not related to the RE, because this
262 parameter should be similar in both cases.

263 A second possible cause is the blocking effect of the RE, which has not been considered in
264 equilibrium EIS measurements.^{23,33} The proposed 2D electrochemical model provides insight into
265 the blocking effect of the RE and a quantitative discussion of errors during dynamic

266 measurements.

267 Electrolyte concentration distribution around the RE during a 3200 s discharge followed by a 1800
268 s rest period is demonstrated in Fig. 7, where the anode, separator, and cathode are shown from
269 left to right. Lithium ion transport from one electrode to another is blocked by the RE, which acts
270 as a physical barrier and increases the electrolyte concentration on the anode side and decreases
271 that on the cathode side. The maximum difference between the electrolyte concentration in the
272 blocked area and that at the same x-axis coordinate in the unblocked area, $(\Delta C_e)_{\max}$, increases with
273 time. The difference increases to about 1700 mol/m³ at 3000 s and decreases to about 417 mol/m³
274 at 5000 s. The blocked area extends about 0.2 mm beyond the edge of the RE, which has a width
275 of 0.4 mm.

276 The average solid-phase composition of the anode during discharge is shown in Fig. 8. Anode
277 particles in the blocked area have greater solid-phase concentration than those in the unblocked
278 area. Consequently, lithium deintercalation of particles in the blocked area is driven primarily by
279 the solid-phase concentration gradient, which impedes the flow of current between the two
280 electrodes. However, unlike the electrolyte, the maximum difference in solid-phase concentration
281 between the blocked and unblocked regions at the same x-axis displacement, $(\Delta C_{s,\text{avg}})_{\max}$, does not
282 increase. $(\Delta C_e)_{\max}$ equals 3267, 4169, and 3755 mol/m³, respectively, at 1000s 2000 s and 3000 s.

283 During the rest period after 3200 s, $(\Delta C_e)_{\max}$ decreases gradually with time to reach an equilibrium
284 state, which indicates that the solid-phase lithium in the blocked area diffuses across the
285 concentration gradient to the particles in the remaining area. This is not strictly a physical
286 diffusional process, in which the electrolyte bridges between different particles, because the bulk
287 solid-phase potential is nearly uniform over the entire region of the electrode. Thus, the abnormal

288 potential relaxation behavior results from the difference in electrolyte potential adjacent to and
289 remote from the RE.

290 The internally positioned RE not only blocks Li^+ transport in the electrolyte phase, but also
291 inhibits the electrode reaction in the blocked area, which causes the active material there to exhibit
292 hysteresis. This condition leads to an increase in the abnormal potential during the rest period. The
293 anode of Cell B is partially blocked by the RE during discharge, when a solid-phase concentration
294 gradient is established along the y-axis. The gradient accumulates during the discharging/charging
295 process and diminishes during the subsequent rest period.

296 The overall current density at the anode is zero during rest, which means that the local current
297 density is small. Thus, the local anode potential is described by:

$$\phi_s - \phi_e \approx U_{\text{eq}} \left(\frac{c_{s,\text{surf}}}{c_{s,\text{max}}} \right) \quad (10)$$

298 Lithium diffusion from the blocked to the unblocked area produces a continual decrease in the
299 solid-phase concentration in the blocked area leading to an increase in the equilibrium voltage, U_{eq} .
300 The measured anode potential, V_a , increases with increasing U_{eq} , which is the origin of the
301 abnormal feature. The 2D model replicates this process in good agreement with experimental
302 results as shown in Fig. 5 and Fig. 6. The cell parameters used in the simulation are listed in [Table](#)
303 [1](#). The different increases in anode potential observed for different final states of charge also are
304 explained by this model. The differential curve of graphite is shown in Fig. 9. The slope is greater
305 at low SOC than at high SOC, which indicates that the shift in U_{eq} is greater at constant lithium
306 diffusion.

307 **3.4 Parameter influence:**

308 The parameters established for electrode potential measurements significantly influence their

309 accuracy, especially under dynamic CC charging or discharging conditions. The accuracy of the
310 electrode potential data cannot be established simply by comparing the terminal voltage to the
311 difference between the anode and cathode potentials. Thus, three different widths, thicknesses, and
312 current rates were considered to examine their impact on the errors caused by the blocking effect.
313 An overview of the parameters selected is given in [Table 2](#). The minimum width of the RE is 25
314 μm , which is on the order of the diameter of the attached Cu wire. The maximum width is similar
315 to the width of the Ni-Li RE.

316 **3.4.1 Width:**

317 To evaluate the effect of RE width on the measurement, a CC charge simulation was carried out
318 for widths of 25, 300, and 800 μm . The simulation involves a CC charge starting from 0.8 SOC to
319 an upper cut-off voltage of 4.2 V followed by 1800 s rest period. The average solid-phase
320 concentration and electrode potential are represented in Fig. 10. To obtain a more explicit
321 comparison, we generated a normalized concentration by removing the absolute change in solid
322 concentration to show relative differences along the y- and x-axis coordinates at the
323 electrode/separator interface.

324 Maxima in the normalized concentration profiles can be explained by the blocking effect of the
325 RE. Greater RE widths correspond to more significant peaks in the concentration differences as
326 shown in Fig. 10 (a) and (c). At the cathode, solid concentrations in the blocked area are greater
327 than in the unblocked area, and the maximum concentration differences are 35, 1514, 3556
328 mol/m^3 at widths of 25, 300, and 800 μm , respectively. The area affected by blocking increases
329 with increasing width. Fig. 10 (b) shows that the measured cathode potential decreases
330 dramatically below its real value causing an unanticipated measurement error. The error between

331 the measured and real cathode potential is 2, 11, and 27 mV at widths of 25, 300, and 800 μm ,
332 respectively. The difference in the solid concentration diminishes progressively during the rest
333 period, as does the error in the measured cathode potential. The solid concentration at the anode is
334 less in the blocked than in the unblocked area consistent with the hysteresis of intercalation.
335 Likewise, the measured anode potential is less than its true value, which indicates that lithium
336 deposition may be overestimated under some conditions during measurement. For example, if a
337 battery with an 800- μm -wide RE is charged from 0.8 SOC at 1/3 C, experimental data indicate
338 that lithium deposition will occur within 1380 s as the measured anode potential reaches 0 V vs
339 Li/Li^+ , not as shown in Fig. 10 (d).

340 **3.4.2 Thickness**

341 Fig. 11 shows the cathode and anode potentials at various RE thicknesses using the same charging
342 protocol as in section 3.4.1. The measured potential is less than the anticipated value for both the
343 cathode and the anode at each thickness. When the RE thickness is 5 μm , the average maximum
344 error of the anode and cathode potentials is 8 mV. The maximum error increases only by 4 and 7
345 mV at thicknesses of 20 and 100 μm , respectively. Thus, thickness has a less significant influence
346 than width, which is the more important factor to be considered. **Please note that there is a gap**
347 **between the positive and negative electrodes where the RE is inserted, leading to deformation of**
348 **the electrodes. Little difference of the positive and negative electrode potentials is seen between**
349 **the gap is considered or not in simulation. For this reason, the deviation caused by gap is**
350 **neglected for brevity. The deviation may become larger for larger width.**

351 **3.4.3 C-rate**

352 Although the C-rate is not a RE parameter, its impact should be assessed. A greater C-rate generally
353 requires a smaller RE. Fig. 12 shows the results of electrode potential measurements with and
354 without a RE. The average maximum errors of the anode and cathode potentials become negligible

355 at small C-rates as shown in Fig. 12. Thus, the electrode potential data are close to anticipated values
356 under thermodynamic or quasi-equilibrium conditions, such as during EIS measurements or low
357 C-rate tests. However, the average maximum errors of the anode and cathode potentials become 11
358 and 37 mV when the C-rate increases to 1/3 and 1 C, respectively. Therefore, data obtained from
359 dynamic tests at high C-rates must be scrutinized carefully to ensure their validity.
360

361 **Table 3** summarizes the average errors of measured electrode potentials produced by simulation
362 with different charging and discharging parameters. At widths of 25 and 300 μm , the average error
363 is less than 15 mV under all conditions, which is an acceptable value. However, the average error
364 at 800 μm increases to 76.5 mV during discharge, which invalidates these experimental data.
365 Thickness dependent errors are less than 15 mV in all cases except at a 100 μm thickness during
366 discharge. Average electrode potential errors during charging and discharging are relatively
367 consistent at all C-rates. Errors are less than 15 mV at C-rates below 1/3 C, although the error
368 exceeds 15 mV at 1 C. The foregoing results provide important principles for proper application of
369 REs. Our findings suggest that a conductive, mesh-like material with a proper proportion of
370 skeleton and pores is an ideal RE substrate that is capable of reducing the blocking effect while
371 loading enough lithium for long-term use. The performance of a RE with this design is being
372 investigated by our group.

373 **4. Conclusions**

374 **A new RE design with improved stability and lifetime is proposed for use in lithium-ion batteries.**
375 **The proposed Ni-Li composite RE can load more lithium than traditional Cu-wire-Li REs. In**
376 **addition, the molten lithium infusion technique strengthens the attachment between the Ni**
377 **substrate and lithium metal and prolongs RE lifetime. More insights into battery behavior can be**
378 **obtained by use of a Ni-Li composite reference electrode of appropriate size.** The impact of Ni-Li
379 RE dimensions on electrode potential measurement were investigated in dynamic tests and
380 evaluated on the basis of experimental results and a 2D electrochemical FEM. Abnormal
381 deviations in negative/positive electrode potentials were observed in dynamic tests during the rest
382 period following discharging/charging and were interpreted in terms of blocking by the internal

383 RE. The internal RE physically blocks the surrounding Li-ion flow during charging and
384 discharging and slows the electrochemical reaction of particles in the blocked area. This behavior
385 introduces hysteresis and produces errors in electrode potential measurements. The abnormality
386 arising from the blocked effect is reproduced by the 2D FEM. Characteristic lengths, widths, and
387 thicknesses of the internal RE were analyzed by the FEM to quantify the errors caused by the
388 blocking effect. The influence of current rate during dynamic tests also was evaluated. The salient
389 conclusions of our investigation are as follows:

390 1) An internal RE with a width of less than 0.3 mm is sufficient to ensure an electrode potential
391 measurement error of less than 15 mV.

392 2) An internal RE with a thickness of less than 0.02 mm is sufficient to ensure an electrode
393 potential measurement error of less than 15 mV.

394 3) When using a 0.3-mm-wide and 0.02-mm-thick internal RE, an applied current rate equal to or
395 less than $1/3$ C will produce an electrode potential measurement error equal to or less than 15 mV.

396 Although specific errors may vary for different battery geometries or electrochemical
397 characteristics, the method described here is useful in analyzing the blocking effects of an internal
398 RE.

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404

Table 1 Electrochemical properties and geometry parameters of the model

Parameter	Anode	Separator	Cathode
Thickness L (m)	52×10^{-6}	25×10^{-6}	50.6×10^{-6}
Solid phase conductivity σ_s ($S \cdot m^{-1}$)	100^{34}		100^{34}
Solid phase porosity ε_s	0.63^b		0.51^b
Electrolyte phase conductivity κ ($S \cdot m^{-1}$)	$\kappa = 0.0911 + 1.9101 \times 10^{-3} c_e - 1.052 \times 10^{-6} c_e^2 + 0.1554 \times 10^{-9} c_e^3$		
Electrolyte phase porosity ε_e	0.3^b	1^b	0.3^b
Solid diffusion coefficient D_s ($m^2 \cdot s^{-1}$)	$2.5 \times 10^{-14} (1.5-x)^{3.5}$ ³⁵ where x=SOC		2×10^{-14} ³⁵
Electrolyte diffusion coefficient D_e ($m^2 \cdot s^{-1}$)	1.5×10^{-10} ³⁵		
Particle radius R_s (m)	2×10^{-6} ³⁶		3×10^{-6} ^a
Charge transfer coefficient α	0.5 ³⁶		0.5 ³⁶
SEI film resistance R_{SEI} ($\Omega \cdot m^2$)	0.01 ³⁶		0 ³⁶
Reaction rate k ($m \cdot s^{-1}$)	8×10^{-12} ^a		5.3×10^{-12} ^a
maximum theoretical concentration $c_{s,max}$ ($mol \cdot m^{-3}$)	31363 ³⁷		51385 ³⁷
Faraday constant F ($C \cdot mol^{-1}$)	96485		
Transference number t_+^0	0.363 ^a		
Initial electrolyte concentration $c_{e,0}$ ($mol \cdot m^{-3}$)	1200 ^a	1200 ^a	1200 ^a

406

^a Assumed.

407

^b Fitted.

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Table 2 An overview of the parameter sets applied in simulation for evaluation of the deviation caused
by RE

Parameters	Width / μm	Thickness / μm	C-rate / C
Width	25	20	1/3
	300	20	1/3
	800	20	1/3
Thickness	300	5	1/3
	300	20	1/3
	300	100	1/3
C-rate	300	20	1/20
	300	20	1/3
	300	20	1

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413 **Table 3 An overview of the deviation caused by RE using different widths, thicknesses and C-rates**

Errors / mV		Width / μm			Thickness / μm			C-rate / C		
		25	300	800	5	20	100	1/20	1/3	1
CHA	Neg	0.6	6.4	26.6	4.7	6.4	9.5	0.8	6	21.1
	Pos	1.1	5.9	16.2	4.4	5.9	6.6	0.7	5.5	18.8
	Average	0.85	6.15	21.4	4.55	6.15	8.05	0.75	5.75	19.95
DCH	Neg	0.3	10.3	54.5	6.7	10.3	13.3	1.2	7.7	22.2
	Pos	6.2	12.5	98.5	11.9	12.5	35.8	1.3	8.1	24.5
	Average	3.25	11.4	76.5	9.3	11.4	24.55	1.25	7.9	23.35

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416 Fig. 1 Schematic illustration of the RE set-ups used in this study: (a) Cu-wire-Li RE, (b) Ni-Li
417 composite RE.

418 Fig. 2 Schematic illustration of the 2D model geometry: 3D view (left) and cross section (right) with
419 a inserted Ni-Li composite RE (white rectangle area) between the electrodes of the cell sandwich.
420 The 2D model is constructed on the cross section.

421 Fig. 3 Cathode (blue solid line) and anode (green solid line) potentials in the cells with (a) the RE of
422 Set-up A and (b) the RE of Set-up B during the C-rate tests. Zoomed views of the potentials during
423 the rest period are shown to highlight the abnormal relaxation potential.

424 Fig. 4 A comparison of the anode/cathode potential profile during the rest period following a
425 discharge/charge : (a) a normal profile, (b) an abnormal profile.

426 Fig. 5 A comparison between the experimental data and model prediction for (a) cell voltage and (b)
427 anode potential in the cell with the RE of Set-up B, during a discharge to 0 SOC, followed by a 1 h
428 rest period.

429 Fig. 6 A comparison between the experimental data and model prediction for (a) cell voltage and (b)
430 anode potential in the cell with the RE of Set-up B, during a discharge to 0.2 SOC, followed by a 3
431 h rest period.

432 Fig. 7 Evolution of distribution for the electrolyte concentration at the adjacent region to the RE
433 during a 3200s discharge at 0.5 C rate, followed by a 1800 s rest period.

434 Fig. 8 Evolution of distribution for the average solid phase concentration at the adjacent region to
435 the RE during the same 3200s discharge at 0.5 C rate and the following 1800 s rest period in Fig. 7.

436 Fig. 9 Equilibrium potential of the graphite anode (top) and its differential potential (bottom).

437 Fig.10 (a) Debiased average solid concentration along y-axis at the cathode/separator interface, (b)
438 cathode potential, (c) debiased average solid concentraon along y-axis at the anode/separator
439 interface, and (d) anode potential during a CC charge at 1/3 C to 4.2 V and a following 1800 s rest
440 period for different widths of the RE.

441 Fig. 11 (a) Cathode potential and (b) anode potential during a CC charge at 1/3 C to 4.2 V and a
442 following 1800 s rest period for different thicknesses of the RE.

443 Fig. 12 A comparison for the deviation caused by the RE at various C-rates. (a) Cathode potential
444 and (b) anode potential during a 1000 s CC charge at different C-rates from 0.5 SOC, followed by a
445 1000 s rest period.

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