Analysis of Electrolyte Imbibition through Lithium-Ion Battery Electrodes

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Abstract: A quantitative measurement of wettability between the porous electrode and the electrolyte in lithium-ion batteries can greatly improve our understanding of wetting behavior. Although the wetting balance method is widely used to measure the electrolyte transport rate in the porous electrodes, it suffers from several drawbacks and has limited accuracy. We here presented a combined experimental and theoretical investigation of the dynamics of electrolyte imbibition through electrodes. We proposed a novel method to accurately measure the electrolyte imbibition rate. Excellent agreement between the experimental data and the developed analytical model is obtained. The coefficient of penetrance (COP) and the solid permeability coefficient (SPC) are identified as important parameters, i.e., the electrolyte with higher COP value wets faster into an electrode, whereas for an electrolyte, the electrode with higher SPC value is more amenable to be impregnated. The effect of electrolyte salt concentration and electrolyte solvent has been studied in detail. The result suggests that increasing salt concentration adversely influences electrolyte wetting rate, whereas switching from EC-DEC system to EC-EMC system improves electrolyte wetting rate. In addition, for the electrolytes tested in this study, the imbibition into the uncalendered graphite anode is much faster than that into the uncalendered NMC532 cathode.

1. Introduction

One of the most critical processes in the manufacturing line of lithium-ion batteries is the formation process, during which an electronically passive film known as the solid electrolyte interface (SEI) layer is created by the decomposition products of the electrolyte solvent molecules and lithium salt [1]. To form stable SEI layers covering all the anode/cathode surface area and to ensure good lithium ion conductivity and rate capability, complete wetting of the electrode and separator pores is essential.

The electrolyte wetting and SEI formation steps pose an unacceptable process time bottleneck and thus add substantial capital cost to a battery production plant. According to Wood et al. [2], the formation process is one of the most expensive processes during battery manufacturing, which typically takes up to several days or weeks depending on the cell chemistry, requiring a large number of battery cyclers and environmental chambers to be installed, large floor space, as well as a tremendous amount of low-grade heat and electricity. Several studies have been conducted to reduce the formation time [3, 4, 5, 6]. According to Lee et al. [4],

1
the formation time can be significantly reduced by skipping the high state-of-charge region. However, this approach generally leads to a decrease in capacity retention. According to Bhattacharya and Alpas [6], the formation time can be markedly shortened by increasing C-rates at the expense of less uniform distribution of the SEI layer, leaving large regions of graphite electrode surface uncovered.

On the other hand, theoretical or experimental investigation of electrolyte wettability of electrodes has rarely been reported, although rapid and complete electrolyte wetting is extremely beneficial for reducing the formation time and achieving higher product quality. Wettability is influenced by the properties of both the liquid electrolyte, such as viscosity and surface tension, and the porous electrode, such as porosity and microstructures. A quantitative measurement of wettability between the porous electrode film and the electrolyte can help us identify the factors that could potentially lead to rapid and complete wetting, greatly improving our design of both the electrode and electrolyte materials.

The wetting balance method is widely used to measure the electrolyte transport rate in porous electrodes [7, 8, 9, 10], which is performed gravimetrically with an immersion testing system to track sample mass during the liquid infiltration process. The electrode sample is suspended under a high-precision balance and a container of liquid is lifted to immerse the sample to a set depth, as schematically shown in Fig. 1(a). The balance records the mass increase of electrolyte inside of the electrode film as a function of time. The Lucas-Washburn equation [11, 12] is then used to analyze the relation of mass increase with time:

\[
\frac{\Delta m}{\rho A} = h(t) = K \sqrt{t} \quad (1a)
\]

\[
K = \sqrt{\frac{\sigma \cos \theta}{2 \mu}} \quad (1b)
\]

where \( \Delta m \) is the mass increase, \( \rho \) is the density of the electrolyte, \( A \) is the cross-section area of the electrode, \( \epsilon \) is the porosity of the electrode, \( h \) is the height of the rising electrolyte, \( t \) is the passed imbibition time, \( r_e \) is the effective pore radius of the electrode, \( \sigma \) is the surface tension of the electrolyte, \( \theta \) is the intrinsic contact angle of the electrolyte with the electrode, \( \mu \) is the viscosity of the electrolyte, and the parameter \( K \) is a measure for the speed of wetting, which can be obtained from a linear regression of the \( \Delta m \) versus \( \sqrt{t} \) plot. Note that the quantity \( \sigma \cos \theta/(2 \mu) \) is called the coefficient of penetrance and denoted as \( COP \), which represents the penetrativity of the liquid [11].

However, this classical method has limited accuracy [13, 14], which often makes it difficult to use in developing a quantitative understanding of wettability between the porous electrode film and the electrolyte. First, in deriving Eqn. (1a) and (1b), inertia and gravity influences are neglected, although the electrolyte is absorbed into the electrode vertically by capillary force. Second, the process of evaporation occurs simultaneously with imbibition, which could also lead to erroneous results, since the rate of electrolyte evaporation is usually very high. Third, when the measured mass increase during the imbibition process is converted to the height increase, the propagation of the wetting front is assumed to be uniform across the electrode width, and both the cross-section area and the porosity of the electrode are assumed to be uniform along its length; however, any of the assumptions may not be valid in practice. In addition, when the electrode is brought into contact with the electrolyte, a capillary bridge forms, resulting in a sudden decrease in the measured mass, which should be properly subtracted during the mass-to-height conversion.

In this study, an innovative technique based on in-plane liquid imbibition into a thin porous medium is proposed, in which direct visualization of the imbibition front is used for analysis and no mass-to-height conversion is needed. Instead of assuming a uniform wetting front at any instant of time, non-uniform propagation front can be easily identified by direct visualization of the imbibition process. Since the electrolyte is absorbed into the electrode horizontally by capillary force, the effect of gravity can be safely neglected. In addition, the electrode film is sandwiched between a substrate and an overlying surface mask
that suppresses evaporation. Excellent agreement between the experimental data and the developed analytical model is obtained, which demonstrates the robustness and accuracy of the proposed technique.

To answer the following questions quantitatively, we have carried out a series of well-controlled electrolyte imbibition tests on various electrode films using the proposed technique: How do electrolyte salt concentration and electrolyte solvent affect the electrolyte properties? Which electrode has the faster electrolyte wetting rate, anode or cathode? What is the correlation among electrolyte wetting rate, electrolyte surface tension and electrode surface energy? How to correlate electrolyte wetting to electrode properties and predict electrolyte wetting with any given electrolyte formulation? Since the proposed method overcomes the limitations of the classical wetting balance method and provides a better understanding of electrolyte transport in porous electrodes, it greatly helps optimize electrolyte formation and electrode design to achieve rapid and complete wetting, potentially leading to reduced battery production costs and improved product quality.

2. The Proposed Method and Theoretical Analysis
2.1. Experimental Set-up of the Proposed Technique

The proposed method based on in-plane liquid imbibition into a thin porous medium is schematically depicted in Fig. 1(b). The thin electrode film is sandwiched between a transparent substrate made of polyethylene terephthalate (Mylar) and an overlying surface mask made of electrolyte-proof polyethylene (adhesive tape). A small circular hole of radius \( r_0 \) has been cut in the middle of the surface mask. When an electrolyte droplet is placed on the circular hole, the electrode pores imbibe the electrolyte by capillary force. The droplet is large enough to provide sufficient electrolyte for the duration of the experiment. During the imbibition process, the contact area between the electrolyte and the electrode surface is kept constant and equal to the area of the circular hole.

![Figure 1. Schematic of the experimental set-up for (a) the classical wetting balance method and (b) the proposed in-plane imbibition method.](image)

The whole imbibition process is recorded by optical cameras from the top view, the side view, and the bottom view. Since the droplet spreads on top, the results obtained from the bottom view are used for analysis. Small amount of fluorescent dye is added to electrolytes to enhance visualization of the imbibition process. The properties of the electrolyte samples with and without fluorescent dye are carefully measured and compared.

For visualization purpose, the substrate used in this study has to be transparent. To make sure that the change of the substrate material can be safely excluded as a possible factor influencing the imbibition process, the electrode samples used in this study are coated on both copper current collectors and transparent
Mylar substrates, respectively. For the samples coated on copper current collectors, the imbibition process is recorded by an infrared camera from the top view, with the wetted portion of the electrode easily identified due to the temperature differential between the wetted and the unwetted portions, and the testing results are then compared with those obtained from the samples coated on transparent Mylar substrates.

Since the length, $l$, and the width, $w$, of the electrode are both much larger than its thickness, $b$, the imbibition process is considered as purely radial imbibition. To verify if the effect of the sample thickness can be neglected, i.e., if the propagation of the wetting front is uniform across the electrode thickness, the results obtained from the top view using the infrared camera are compared with those obtained from the bottom view using the optical camera.

### 2.2. Theoretical Analysis

The liquid flows through porous media are generally described by Darcy’s law that relates the flow rate with the pressure drop, material permeability and liquid viscosity [15, 16]. For the process of in-plane liquid imbibition into a thin porous medium, the Darcy’s law gives [16]:

$$ q = \frac{Q}{A} = -\frac{k}{\mu} \nabla p \quad (2) $$

where $q$ is the flux, $Q$ is the total discharge in unit time, $A$ is the cross-section area, $\mu$ is the viscosity of the liquid, $k$ is the permeability of the porous medium, and $\nabla p$ is the pressure gradient vector.

For the case of purely radial imbibition, if the pores are distributed uniformly throughout the material and thus the wetted region is radially symmetrical around the center, Eqn. (2) can be simplified as:

$$ q = \frac{Q}{2\pi rb} = -\frac{k}{\mu} \frac{dp}{dr} \quad (3a) $$

which can be re-arranged into the following form:

$$ \frac{Q}{r} \frac{dr}{r} = -2\pi b \frac{k}{\mu} \frac{dp}{d\theta} \quad (3b) $$

where $b$ is the electrode thickness and $r$ represents the radius of the impregnated region. Integration on both sides of Eqn. (3b) yields the following equation:

$$ Q = 2\pi b \frac{k}{\mu} \ln\left(\frac{p_0 - p}{r_0}ight) \quad (3c) $$

where the flow source at the center is assumed to have initial radius $r_0$ and pressure $p_0$. Remember that $r_0$ is the radius of the circular hole on the top surface mask, as shown in Fig. 1(b).

On the other hand, $Q$ can be written as:

$$ Q = \epsilon A v \quad (4) $$

where $\epsilon$ is the porosity of the porous medium and $v$ represents the average penetration velocity [17]. Substituting Eqn. (4) into Eqn. (3c) yields the following equation:

$$ \epsilon(2\pi rb) \frac{dr}{dt} = 2\pi b \frac{k}{\mu} \frac{p_0 - p}{\ln(r/r_0)} \quad (5a) $$

which can be re-arranged as:

$$ r \ln(r/r_0) dr = \frac{k}{\epsilon \mu} (p_0 - p) dt \quad (5b) $$
Since the pressure difference $p_0 - p$ is only associated with capillary pressures and does not depend on time, assuming that when $t = t_0$, $r = r_0$, integration of both sides of Eqn. (5b) yields the following form:

$$\frac{1}{4}r^2[2\ln(r/r_0) - 1] + \frac{1}{4}r_0^2 = \frac{k}{\epsilon\mu}(p_0 - p)(t - t_0) \quad (6a)$$

Assume that $t_0 = 0$, i.e., the time starts when the radius of the impregnated region is equal to the radius of the circular hole, $r_0$. Denoting that $\Delta p = (p_0 - p)$ and $D = \frac{2k\Delta p}{\epsilon\mu}$, Eqn. (6a) can be written as:

$$f(r) = \frac{1}{2}r^2[2\ln(r/r_0) - 1] + \frac{1}{2}r_0^2 = Dt \quad (6b)$$

Eqn. (6b) shows that this model predicts a linear relationship between $f(r)$ and $t$, whose slope gives the imbibition coefficient $D$.

From Eqn. (6b), it can be seen that the larger the $D$ is, the faster the wetting of liquid within the porous medium. The value of $D$ depends on the properties of both the liquid and the porous medium. In this case, the only driving pressure is the capillary pressure that can be written as [11, 16]:

$$\Delta p = \frac{2B\sigma\cos\theta}{r_e} \quad (7)$$

where $B$ is the capillary geometrical coefficient [18], which is equal to one for cylindrical pores and less than one for noncylindrical pores [19], $\sigma$ is the surface tension of the liquid, $\theta$ is the intrinsic contact angle of the liquid with the porous medium, and $r_e$ is the effective capillary radius of the porous medium. Substituting Eqn. (7) into the expression for $D$, the following form can be obtained:

$$D = 4\left(\frac{\sigma}{\mu}\right)\frac{kB}{\epsilon r_e} \cos\theta \quad (8a)$$

in which the first term $\sigma/\mu$ solely depends on the properties of the liquid, the second term $kB/(\epsilon r_e)$ only depends on the properties of the porous medium, and the third term $\cos\theta$ is a liquid-solid interface property.

Since the quantity $\sigma\cos\theta/(2\mu)$ is called the coefficient of penetrance and denoted as $COP$ [11], Eqn. (8a) can be alternatively written as:

$$D = 8[COP]\left(\frac{kB}{\epsilon r_e}\right) \quad (8b)$$

which shows that, for a porous medium, the $D$ value is proportional to the $COP$ value of the liquid, i.e., the liquid with higher $COP$ value wets faster into the porous medium.

We here introduce a new quantity $kB\cos\theta/(2\epsilon r_e)$, called the solid permeability coefficient and denoted as $SPC$. $SPC$ has unit of length and it represents a property of the porous medium related to its intrinsic permeability. The higher the value of $SPC$, the more amenable the porous medium to be percolated by the liquid. Eqn. (8a) can then be alternatively written as:

$$D = 8[SPC]\left(\frac{\sigma}{\mu}\right) \quad (8c)$$

which shows that, for any type of liquid, the $D$ value is proportional to the $SPC$ value of the porous medium, i.e., the liquid wets faster in the porous medium with higher $SPC$ value.
2.3. Experimental Procedures

In this study, to investigate the effect of electrolyte salt concentration and electrolyte solvent, two solvent systems are studied, one with two and the other with five different salt concentrations. The $D$ value for each electrode/electrolyte combination is measured; the $COP$ value for each type of electrolyte is obtained; and finally, the SPC value for each type of electrode is obtained and compared.

The $D$ value for each electrode/electrolyte combination is obtained based on Eqn. (6b). Based on the experimental measurements of $r$ and $r_0, f(r)$ can be plotted versus $t$, and then the value of $D$ can be obtained by performing a linear regression of the $f(r)$ versus $t$ plot.

To obtain the $COP$ value of each type of electrolyte, the surface tension of the electrolyte, $\sigma$, the viscosity of the electrolyte, $\mu$, and the intrinsic contact angle of the electrolyte with the electrode, $\theta$, are all needed. While the values of $\sigma$ and $\mu$ can be measured directly using a tensiometer and a rheometer, respectively, it is not so straightforward to obtain the value of the intrinsic contact angle $\theta$, but this issue has been carefully investigated in our previous publication [20] and briefly summarized as follows.

The surface of the electrode samples deviates from ideal surfaces due to its roughness, porosity, and heterogeneity. Such deviation from ideality results in an apparent contact angle $\theta^*$ differing from its intrinsic contact angle $\theta$ [20, 21]. The Wenzel [22] and Cassie–Baxter [23] models are often used to relate the apparent contact angle $\theta^*$ to the intrinsic contact angle $\theta$ if the surface roughness ratio $fr$ and the surface solid-area fraction $fs$ are given. In this study, following the previous researchers [21, 24, 25], the advancing contact angle $\theta_i$ is used as the apparent contact angle $\theta^*$, which is measured using a volume-changing method. The surface roughness ratio $fr$ is measured using an optical profilometer, and the surface solid-area fraction $fs$ is calculated using an analytical method proposed in our previous paper [20]. The intrinsic contact angle $\theta$ is then obtained based on the values of $fs, fr,$ and $\theta^*$ by using the Wenzel and Cassie–Baxter models following the procedures provided in our previous paper [20].

Finally, the SPC value of each type of electrode is obtained by plugging into Eqn. (8c) the experimentally measured $D$ values and the $\sigma/\mu$ values. The $SPC$ value is obtained by performing a linear regression of the $D$ versus $\sigma/\mu$ plot.

3. Materials and Methods

3.1. Electrode Sample Fabrication and Preparation

Materials used in electrode fabrication are listed in Table S1 in Supplementary Information. Three different types of electrodes were fabricated for this study. The first two types were NMC532 and A12, respectively, processed with NMP as solvent and coated via doctor blade on polyethylene terephthalate (Mylar) substrates. The third type was A12 processed with NMP as solvent and coated via doctor blade on copper current collectors. As received NMC532 powder (particle size distribution D50 value approximately 11 µm and Brunauer–Emmett–Teller surface area approximately 0.3 m$^2$/g), Denka CB (powder grade), and 5130 PVDF were used in preparing NMC 532 electrodes. The components of A12 electrodes include A12, C65 CB, and 9300 PVDF. The thickness of the Mylar substrate and the copper current collector is approximately 15 µm and 9 µm, respectively.

<table>
<thead>
<tr>
<th>Electrode (Thickness)</th>
<th>Solvent</th>
<th>Fabrication Process (Bulk Porosity)</th>
<th>Electrode Composition</th>
<th>Substrate (Thickness)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMC532-Mylar (49 µm)</td>
<td>NMP</td>
<td>Uncalendered (55% ± 2.5%)</td>
<td>NMC532/Denka CB/5130 PVDF in 90/5/5 wt%</td>
<td>Mylar (15 µm)</td>
</tr>
</tbody>
</table>
A12-Mylar (76 µm) | NMP | Uncalendered (55% ± 1.9%) | A12/C65 CB/9300 PVDF in 92/2/6 wt% | Mylar (15 µm)
---|---|---|---|---
A12-Copper (76 µm) | NMP | Uncalendered (55% ± 1.3%) | A12/C65 CB/9300 PVDF in 92/2/6 wt% | Copper (9 µm)

The electrode fabrication process follows the standard procedure which has been reported previously [20, 26]. Electrode slurry was prepared by a planetary mixer (Ross Laboratory Mixers & Blenders, Hauppauge, NY, USA). The thickness of the NMC532 and A12 electrodes (including the thickness of the substrate) is approximately 49 µm and 76 µm, respectively. Table 1 lists the detailed information for the three types of electrodes used in this study.

Electrode samples were then cut into 2 cm × 2 cm pieces. A surface mask made of electrolyte-proof polyethylene (adhesive tape) was applied to the top surface of the electrode sample. A small circular hole of radius 0.5 mm to 0.7 mm was cut in the middle of the surface mask. Before performing experimental measurements, the electrode samples were kept in vacuum oven at 80°C for 14 hours to remove residual moisture.

3.2. Electrolyte Sample Fabrication and Preparation

Materials used in electrolyte fabrication are listed in Table S2 in Supplementary Information. Electrolytes were mixed inside an argon-filled glove box with appropriate amount of LiPF₆, ethylene carbonate (EC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC) to prepare seven different types of electrolyte. EC was heated and melted before being mixed with EMC or DEC. The EC/EMC or EC/DEC was 3/7 wt%. As shown in Table 2, EC-EMC based electrolytes with five different LiPF₆ salt concentrations ranging from 0.0 M to 1.5 M and EC-DEC based electrolytes with two different LiPF₆ salt concentrations 0.0 M and 1.2 M, respectively, are fabricated for this study.

<table>
<thead>
<tr>
<th>Electrolyte #</th>
<th>LiPF₆ Concentration (M)</th>
<th>Solvent Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0</td>
<td>EC-DEC</td>
</tr>
<tr>
<td>2</td>
<td>1.2</td>
<td>EC-DEC</td>
</tr>
<tr>
<td>3</td>
<td>0.0</td>
<td>EC-EMC</td>
</tr>
<tr>
<td>4</td>
<td>0.6</td>
<td>EC-EMC</td>
</tr>
<tr>
<td>5</td>
<td>1.0</td>
<td>EC-EMC</td>
</tr>
<tr>
<td>6</td>
<td>1.2</td>
<td>EC-EMC</td>
</tr>
<tr>
<td>7</td>
<td>1.5</td>
<td>EC-EMC</td>
</tr>
</tbody>
</table>

The electrolytes were always stored inside the glove box. A small amount of electrolyte was taken from the glove box for the experiments, and the residue was disposed of afterwards.

3.3. Fluorescent Dye Addition

Small amount of fluorescent dye was added to electrolytes to enhance visualization of the imbibition process. 1 wt.% of Rhodamine 6G (Sigma-Aldrich, St. Louis, MO, USA) was dissolved in all the electrolyte samples except for Electrolyte #1 and #3, which were pure solvents and did not dissolve Rhodamine 6G. Instead, 0.5 wt.% of Rhodamine B (Sigma-Aldrich, St. Louis, MO, USA) was dissolved in Electrolyte #1 and #3. To investigate the effect of dye addition, surface tension and viscosity of the electrolyte samples were measured both with and without the fluorescent dye.

3.4. Surface Tension Measurement for Electrolytes
The surface tension of the electrolytes, \( \sigma \), was measured using a BP100 bubble pressure tensiometer (Kruss, Hamburg, Germany). The immersion of the capillary was controlled by software, so the measuring procedure was entirely automatic. An air flow from the capillary produced bubbles in the sample, and a pressure sensor determined the maximum pressure during bubble formation, from which the surface tension was automatically calculated by software.

3.5. Viscosity Measurement for Electrolytes

The viscosity of the electrolytes, \( \mu \), was measured on an AR 1000 rheometer (TA Instruments, New Castle, DE, USA) using cone and plate geometry. A 1.59° aluminum cone and a 6-cm plate were used. A thin layer of liquid with a thickness of approximately 50 \( \mu \)m was formed between the horizontal plate and the cone. The cone then started rotating at different speeds resulting in shear rates in the range of 10 s\(^{-1}\) to 1000 s\(^{-1}\). The shear stress was measured for each specific shear rate. All measurements were performed at 25°C.

3.6. Advancing Contact Angle Measurement

Advancing contact angles, \( \theta_{an} \), for electrode surfaces were measured by using a volume-changing method, i.e., by monitoring the advancing contact angle as the drop volume on the surface was dynamically changed. During the measurements, a small droplet was first formed and placed on the surface. A needle connected to a 500 µL threaded plunger syringe was then brought close to the surface, and by dispensing more liquid from the syringe, the volume of the droplet was gradually increased. The whole process was recorded by a PL-A662 microscopy camera (PixeLINK, Gloucester, ON, Canada). Image processing was then performed using public domain ImageJ software [27]. Each measurement was repeated at least five times to ensure repeatability of the result.

3.7. Surface Roughness Ratio Measurement

The surface roughness ratio, \( fr \), was measured by Wyko NT1100 optical profiling system (Veeco Instruments, Plainview, NY). The software Wyko Vision 32 associated with the instrument was used to create 2D profiles and 3D images of the surfaces as well as calculate true surface area. The magnification of the objective lens used in the measurement was \( \times 10 \).

3.8. Imbibition Process Recording Using Cameras

For the electrode samples coated on transparent Mylar substrates, as the electrolyte droplet spread on top, the imbibition process was recorded by a Kodak MegaPlus ES 1.0 camera (National Instruments, Austin, TX, USA) from the top view, a high-speed Phantom V2011 camera (Vision Research, Wayne, NJ, USA) from the side view, and a Basler avA1000-120km camera (Basler AG, Ahrensburg, Germany) connected to a Zeiss AXIO Observer A1 inverted optical microscope (Carl Zeiss AG, Oberkochen, Germany) from the bottom view. A monochromatic green laser beam generated by a 532 nm diode-pumped solid state lasers (Spectra-Physics, Santa Clara, CA, USA) was used to illuminate the sample coaxially with the Basler avA1000-120km camera’s viewing direction. As the fluorescent dye dissolved in the electrolyte became excited by the laser beam, the entire imbibition process was recorded by the camera. For the electrode samples coated on copper current collectors, the imbibition process was recorded by a FLIR A325sc infrared camera (FLIR Systems, Wilsonville, OR, USA) from the top view. As the infrared camera was not able to retrieve any useful information from samples with top surface mask, only the samples without top surface mask were used for the infrared-related experiments. Image processing was performed using MATLAB R2018a (MathWorks, Natick, MA, USA) and public domain ImageJ software [27]. Five independent imbibition experiments are performed for each electrode/electrolyte combination.

4. Results and Discussion

4.1. Surface Tension and Viscosity of Electrolytes
Surface tension and viscosity of the electrolyte samples with and without fluorescent dye are listed in Table S3 and Table S4 in Supplementary Information, respectively. As shown in Fig. 2(a) and Fig. 2(b), the value of surface tension slightly increases with increasing salt concentration, whereas the value of viscosity substantially increases as the salt concentration is increased. No significant change has been observed after the fluorescent dye is added, indicating that the addition of fluorescent dye has negligible effect on the electrolyte properties.

(a)  
(b)  

(c)  
(d)  

Figure 2. (a) Surface tension and (b) viscosity of electrolyte samples with and without fluorescent dye, respectively. (c) and (d): The values of advancing contact angles $\theta_A$ and intrinsic contact angle $\theta$ for all the electrode/electrolyte combinations.

4.2. Contact Angle of Electrolyte with Electrode

In this study, the advancing contact angle $\theta_A$ is used as the apparent contact angle $\theta^*$, which is different from the intrinsic contact angle $\theta$, due to the electrode surface textures which make them non-ideal surfaces. The Wenzel [22] and Cassie–Baxter [23] models are used to relate the measured apparent contact angle $\theta^*$ to the intrinsic contact angle $\theta$ with the surface roughness ratio $fr$ obtained from optical profilometer measurements and the surface solid-area fraction $fs$ calculated using the analytical method proposed in our previous paper [20]. The electrode surface properties are listed in Table S5 in Supplementary Information. The values of the advancing contact angle $\theta_A$ and the intrinsic contact angle $\theta$ for each electrode/electrolyte combination are listed in Table S6 in Supplementary Information and plotted in Fig. 2(c) and Fig. 2(d), respectively.

4.3. Analysis on Imbibition Coefficient
In our theoretical analysis, we assume that the electrode pores are distributed uniformly throughout the material and thus the wetted region is radially symmetrical around the center. In our experiments, this assumption has been easily confirmed by direct visualization of the imbibition process. Some representative images are shown in Fig. 3.

Figure 3. Snapshots of the imbibition process of the electrolyte #5 into the A12 electrode obtained by the optical camera from the bottom view, showing that the wetted region is radially symmetrical around the center. The time starts when the radius of the impregnated region is equal to the radius of the circular hole on the top surface mask. The first row is the original images obtained from the optical camera, and the second row is obtained after image processing.

Assuming that the time, $t$, starts when the radius of the impregnated region, $r(t)$, is equal to the radius of the circular hole, $r_0$, the time evolution of the radius of the impregnated region can be plotted. Fig. 4(a) shows the $r(t)$ versus $t$ plot for three imbibition experiments of the electrolyte #6 into the A12 electrode, for which the initial radius, $r_0$, is equal to 0.52 mm, 0.58 mm, and 0.70 mm, respectively.

Substituting the experimentally measured values of $r$ and $r_0$ into the left-hand side of Eqn. (6b), $f(r)$ can be plotted versus $t$. Fig. 4(b) shows the corresponding $f(r)$ versus $t$ plot for the three imbibition experiments. Linear regression is then performed, which renders the coefficient of determination $R^2=1.00$. Therefore, as predicted by Eqn. (6b), a perfectly linear relationship between $f(r)$ and $t$ is experimentally obtained, indicating excellent agreement between the experimental data and the developed analytical model.

The value of the imbibition coefficient, $D$, is then obtained as the slope of the linear regression line, which is equal to $1.10e^{-7}$ m$^2$/s, $1.14e^{-7}$ m$^2$/s, and $1.20e^{-7}$ m$^2$/s, respectively. It can be seen that, due to material variation in the electrode samples, sometimes slightly different slopes can be obtained from the experiments performed on the same electrode/electrolyte combination.

Five independent imbibition experiments were performed on each electrode/electrolyte combination and the average value of $D$ was obtained for each case. Fig. 4(c) to Fig. 4(f) shows the representative curves for both the $r(t)$ versus $t$ plot and the $f(r)$ versus $t$ plot for each case. The obtained $D$ values are listed in Table S7 in Supplementary Information.
Figure 4. Three imbibition experiments of the electrolyte #6 into the A12 electrode, for which the initial radius, $r_0$, is equal to 0.52 mm, 0.58 mm, and 0.70 mm, respectively. Here it shows (a) the $r(t)$ versus $t$ plot; and (b) the $f(r)$ versus $t$ plot. Five independent imbibition experiments were performed on each electrode/electrolyte combination. Here it shows the representative curves for (c) the $r(t)$ versus $t$ plot and (d) the $f(r)$ versus $t$ plot for the electrolytes in the NMC532 electrodes; and (e) the $r(t)$ versus $t$ plot and (f) the $f(r)$ versus $t$ plot for the electrolytes in the A12 electrodes. Note that (a), (c), and (e) are drawn directly based on the measurement points. Since the video is captured at twenty frames per second, the data points are so dense that they overlap with each other and form their own lines.

4.4. Effect of Electrode Substrate and Electrode Thickness

Infrared imaging is used to investigate the effect of electrode substrate and electrode thickness. For visualization purpose, the electrode samples used in the imbibition experiments are coated on transparent
Mylar substrates. Therefore, it is important to validate that the effect of electrode substrate on the imbibition process is negligible. For this purpose, some electrode samples are coated on copper current collectors and the imbibition process is recorded by an infrared camera from the top view. The results of the $D$ values are then compared with those obtained from the samples coated on transparent Mylar substrates.

![Figure 5. Snapshots of the imbibition process of the electrolyte #6 into the A12 electrode obtained by the infrared camera from the top view.](image)

Figure 5. Snapshots of the imbibition process of the electrolyte #6 into the A12 electrode obtained by the infrared camera from the top view.

![Figure 6. For the imbibition process of the electrolyte #6 into the A12 electrode, similar $D$ values are obtained from the following three cases: the electrode samples on Mylar substrate recorded from top view using infrared camera; the electrode samples on copper substrate recorded from top view using infrared camera; and the electrode samples on Mylar substrate recorded from bottom view using optical camera.](image)

Figure 6. For the imbibition process of the electrolyte #6 into the A12 electrode, similar $D$ values are obtained from the following three cases: the electrode samples on Mylar substrate recorded from top view using infrared camera; the electrode samples on copper substrate recorded from top view using infrared camera; and the electrode samples on Mylar substrate recorded from bottom view using optical camera.

In addition, since the length and the width of the electrode are both much larger than its thickness, the imbibition process is assumed to be purely radial imbibition. To verify if the effect of the sample thickness can be neglected, the results of the $D$ values obtained from the top view using the infrared camera are compared with those obtained from the bottom view using the optical camera.

Note that the infrared camera is only used for verification purpose. This is because infrared cameras generally suffer from low resolution and high noise-to-signal ratios. In addition, infrared cameras were not able to retrieve any useful information from the electrode samples with top surface mask, so only the samples without top surface mask were used for the infrared-related experiments. Some representative images obtained by the infrared camera from the top view are shown in Fig. 5.

The results show that the $D$ values obtained from top view using infrared camera are very close to those obtained from bottom view using optical camera. For example, for the imbibition process of the electrolyte...
#6 into the A12 electrode, similar $D$ values are obtained from the following three cases: the electrode samples on Mylar substrate recorded from top view using infrared camera; the electrode samples on copper substrate recorded from top view using infrared camera; and the electrode samples on Mylar substrate recorded from bottom view using optical camera, as shown in Fig. 6. The results indicate that the propagation of the wetting front is uniform across the electrode thickness and that the effect of substrate is negligible so that the proposed technique can be extended to electrode samples coated on different substrates.

Figure 7. Regardless of the electrode type, (a) the $D$ value decreases with increasing salt concentration; (b) the $D$ value increases when switching the solvent from EC-DEC to EC-EMC; (c) the COP value decreases with increasing salt concentration; and (d) the COP value increases when switching the solvent from EC-DEC to EC-EMC.

4.5. Effect of Electrolyte Salt Concentration and Electrolyte Solvent

The electrolyte salt concentration could significantly affect the electrolyte properties and its wetting behavior on porous electrodes. The electrolyte #1 and #2 are EC-DEC based electrolytes with two different LiPF$_6$ salt concentrations, 0.0 M and 1.2 M, respectively, whereas the electrolyte #3 to #7 are EC-EMC based electrolytes with five different LiPF$_6$ salt concentrations ranging from 0.0 M to 1.5 M.

Fig. 7(a) shows that, regardless of electrode type and electrolyte solvent, the $D$ value decreases with increasing salt concentration. This result can be predicted based on our theoretical analysis. As shown in Fig. 2(a) and Fig. 2(b), both surface tension and viscosity of the electrolyte samples increase with increasing
salt concentration, but the increase in viscosity is much more significant. Thus, the surface tension to viscosity ratio decreases with increasing salt concentration. As listed in Table S6 in Supplementary Information, the value of \( \cos \theta \) also decreases with increasing salt concentration. Hence, the COP value, i.e., \( \sigma \cos \theta / (2\mu) \), decreases with increasing salt concentration, as plotted in Fig. 7(c) and listed in Table S7 in Supplementary Information. As shown in Eqn. (8b), for an electrode, the \( D \) value is proportional to the COP value of the electrolyte, and thus the \( D \) value is predicted to be decreasing with increasing salt concentration.

This result suggests that minimum amounts of salt should be used in electrolytes to maximize wetting rate. However, an electrolyte with insufficient salt will suffer from low ionic transport capabilities. Hence, the salt concentration needs to be optimized to satisfy the requirements of both fast wetting rate and high ionic transport capability.

While a variety of solvents can be used in electrolytes, using a solvent with advantageous wetting characteristics can help us to achieve rapid and complete wetting. In this study, two common solvent systems, i.e., EC-EMC and EC-DEC [28], are used to investigate the solvent effect on the imbibition rates of electrolytes.

![Figure 8](image)

**Figure 8.** Five independent imbibition experiments were performed on each electrode/electrolyte combination. Here it plots the experimentally measured \( D \) values and the corresponding \( \sigma / \mu \) values for (a) the case of the NMC532 cathode and (b) the case of the A12 anode. The SPC value is obtained as the slope of the linear regression line.

Fig. 7(b) shows that, regardless of electrode type and electrolyte salt concentration, the \( D \) value increases when switching from EC-DEC to EC-EMC. Again, this result can be predicted based on our theoretical analysis. The COP value increases when switching from EC-DEC to EC-EMC for both pure and salt-containing solvents, as plotted in Fig. 7(d) and listed in Table S7 in Supplementary Information, and thus the \( D \) value is predicted to be increasing when switching from EC-DEC to EC-EMC. Hence, EC-EMC is preferred than EC-DEC for enhanced wetting rate in lithium-ion cells.

Liquid electrolyte used in lithium-ion batteries usually consists of binary and trinary solvents, it is possible that there may be selective penetration during the wetting process. One way to investigate this is to measure the imbibition rate of individual solvents as well as that of their mixture. If the imbibition rate of the mixture is the same as that of the fastest individual component, selective penetration may have occurred. However, the goal of this study is to investigate the imbibition rate of typical liquid electrolytes used in lithium-ion batteries regardless of whether or not selective penetration occurs. We investigated two solvent systems, EC-EMC and EC-DEC, with various salt concentrations, which are typical electrolytes used for lithium-
ion batteries. If selective penetration occurs, the COP value is for the fastest component and it still provides critical guidance on cell manufacturing.

In addition, we want to point out that contact angle measurement is a common technique often used to evaluate the wettability between electrolyte and electrode, whereas the technique proposed in this study measures the electrolyte imbibition rate through electrode. It is important to note that these two concepts are different. Contact angle characterizes only surface wettability, and it does not reflect the bulk properties. In contrast, as shown in Eqn. (8a), the imbibition rate not only depends on the contact angle, but also on the properties of the electrolyte, such as viscosity and surface tension, and as well as the properties of the electrode, such as permeability, porosity, capillary geometrical coefficient, and effective capillary radius. Hence, the contact angle measurement alone does not suffice to predict the complete wetting time. As shown in Table S6 in the Supplementary information, the contact angles of all the electrolytes on the NMC532 cathode are smaller than the ones on the A12 anode, indicating better surface wettability of the NMC532 cathode. However, the imbibition of all the electrolytes into the A12 anode is much faster than the one into the NMC532 cathode, implying the significance of the terms other than the contact angle.

### 4.6. Analysis on Solid Permeability Coefficient

Eqn. (8c) shows that, for any type of electrolyte, the D value is proportional to the SPC value of the electrode, i.e., the electrolyte wets faster in the electrode with higher SPC value. The SPC value of each electrode is obtained by plugging into Eqn. (8c) the experimentally measured D values and the $\sigma/\mu$ values.

For each electrode/electrolyte combination, the experimentally measured D values and the corresponding $\sigma/\mu$ values are listed in Table S7 in Supplementary Information and plotted in Fig. 8. Linear regression is then performed, which renders the coefficient of determination $R^2=0.993$ for the case of the NMC532 cathode and $R^2=0.987$ for the case of the A12 anode, respectively. Therefore, as predicted by Eqn. (8c), a linear relationship between D and $\sigma/\mu$ is experimentally obtained, indicating excellent agreement between the experimental data and the developed analytical model. Eqn. (8c) shows that the slope of the linear regression line is equal to 8SPC, and thus SPC is obtained as 9.95e-10 m for the case of the NMC532 cathode and 2.20e-9 m for the case of the A12 anode, respectively.

It can be seen that the SPC value of the A12 anode is more than two times of that of the NMC532 cathode, implying that for the electrolytes tested in this study, the imbibition into the uncalendered A12 anode is much faster than that into the uncalendered NMC532 cathode.

### 5. Concluding Remarks

In this study, we presented a combined experimental and theoretical investigation of the dynamics of electrolyte imbibition through electrodes. We proposed a novel method to accurately measure the electrolyte imbibition rate. Excellent agreement between the experimental data and the developed analytical model has been obtained, which demonstrates the robustness and accuracy of the proposed technique.

The penetrance coefficient, COP, and the solid permeability coefficient, SPC, are identified as important parameters, i.e., the electrolyte with greater COP value wets faster into an electrode, whereas for an electrolyte, the electrode with greater SPC value is more amenable to impregnation. The effect of electrolyte salt concentration and electrolyte solvent has been studied in detail. The result suggests that increasing salt concentration adversely influences electrolyte wetting rate, whereas switching from EC-DEC system to EC-EMC system improves electrolyte wetting rate. In addition, for the electrolytes tested in this study, the imbibition into the uncalendered A12 anode is much faster than that into the uncalendered NMC532 cathode. Note that the COP and SPC values allow us to predict the imbibition rate of any type of electrolyte in porous electrodes, which provides critical guidance on electrolyte formulation, electrode design, and cell manufacturing.
The electrodes tested in this study were uncalendered, but we are definitely aware of the process of calendering and its significant effect on the electrolyte imbibition rate through electrodes. In fact, the novel technique presented in this study can be used to systematically investigate the effect of various manufacturing factors on electrolyte imbibition rate through electrodes, such as calendering degree, slurry formulation, mixing sequences, and wetting temperature, etc. It is also important to explore the effect of aging time on battery performance. These endeavors will be left as our future work.

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