Electrodeposition of Metals and Preparation of Metal Nanoparticles in Nonaqueous Electrolytes and Their Application to Energy Devices

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Graphical Abstract
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Abstract

Nonaqueous electrolytes are used in various electrochemical devices as their electrochemical potential window is wider than that of aqueous electrolytes. Electrochemical reactions significantly change depending on the combination of nonaqueous solvent and salt and the dissolved state of the metal ions or redox species in the solvent. Room-temperature ionic liquids (RTILs), a type of nonaqueous solvent, have unique physicochemical properties such as negligible vapor pressure and non-flammability. Their application as reaction media for a variety of reactions, including electrochemical reactions has attracted significant interest, as they enable reactions that cannot proceed in water or organic solvents. We have been researching materials synthesis and energy devices using RTILs and organic electrolytes. Herein, we comprehensively review our research on the electrodeposition of metals, preparation of metal nanoparticles, and secondary batteries using nonaqueous electrolytes.
1. Introduction

The research and development of electrochemical devices for energy conversion and storage has become increasingly important for the realization of a sustainable society, as they can provide meaningful solutions for the problem of depletion of scarce resources and suggest new approaches for the utilization of renewable energy. With the ubiquity of mobile devices and the commercialization of electric vehicles, the demand for energy devices with large capacities has significantly increased.\(^1,2\) The construction of electrochemical devices requires electrolytes with a wide electrochemical potential window and high ionic conductivity. Hence, polar organic solvents are widely used for the development of electrochemical devices. For example, carbonate-based solvents are widely used as electrolytes in commercial lithium-ion batteries. Nevertheless, room-temperature ionic liquids (RTILs), also known as room-temperature molten salts, have attracted significant attention as a potential nonaqueous electrolyte alternative to organic solvents. RTILs are salts that exist as a liquid below 100 °C and exhibit unique physicochemical properties such as negligible vapor pressure, non-flammability, high ionic conductivity, and excellent chemical stability.\(^3-8\) The first RTIL, ethyl ammonium nitrate, was reported by P. Walden and his group in 1914.\(^9\) However, it is with the discovery of air-stable RTILs comprising onium and fluorinated anions in the 1990s\(^{10,11}\) that RTILs gained considerable traction in basic and applied research in various fields owing to their unique physicochemical properties and ease of handling.\(^12-17\) Because the physicochemical properties of RTILs can be tuned by tailoring the structure and the combination of cation and anion, RTILs with
various structures have been synthesized in the past few decades.\textsuperscript{7} In the field of electrochemistry, the unique electrode-electrolyte interface induced by RTILs, the coordination environment of the metal ions in RTILs, and the physicochemical behavior of RTILs, which are different from that of dilute solutions in the ideal state, still arouse the interest of researchers.\textsuperscript{5,12,14} Furthermore, RTILs are attractive not only as electrolytes but also as reaction media for various chemical reactions such as materials synthesis and organic chemistry and have led to innovative functional materials and material transformation.\textsuperscript{18-20}

Our research focuses on materials synthesis and energy devices using nonaqueous electrolytes, mainly RTILs, as reaction media. Herein, we comprehensively review our fundamental studies on the electrodeposition of metals and preparation of metal nanoparticles using RTILs, design, synthesis, and structure-physicochemical property relationship of RTILs, and secondary batteries using nonaqueous electrolytes.

2. Electrodeposition of Metals and Preparation of Metal Nanoparticles in RTILs

2.1 Metal nanoparticles prepared by RTIL-sputtering method

Over the past few decades, metal nanoparticles have gained significant attention owing to their distinctive characteristics such as specific catalytic activity, large surface area, and quantum size effect.\textsuperscript{21} Metal nanoparticles are generally synthesized by reacting metal salts used as precursors with a reducing agent in the presence of stabilizers to prevent aggregation in a solvent, and the particle size
is controlled by changing the concentration of the reactants and stabilizer.\textsuperscript{22} The synthesis of metal nanoparticles in RTILs has become a hot research topic because RTILs serve as not only a reaction medium but also a stabilizing agent, thereby allowing the homogeneous dispersion of the produced metal nanoparticles.\textsuperscript{13,18,23} Although metal nanoparticles can be prepared in RTILs using metal precursors and reducing reagents as in the case of organic solvents, Torimoto and Kuwabata \textit{et al.} demonstrated that magnetron sputtering is a promising technique for producing metal nanoparticles uniformly dispersed in RTILs without any additional reagents.\textsuperscript{24} This method, called the RTIL-sputtering method, is a simple technique that takes advantage of the negligible vapor pressure of RTILs to produce various metal or metal oxide nanoparticles in RTILs.\textsuperscript{25-30} We prepared Pt nanoparticles by the RTIL-sputtering method and used them as a catalyst in the electrochemical oxygen reduction reaction (ORR) for the cathode of polymer electrolyte fuel cells (PEFCs).\textsuperscript{31-34}

We prepared Pt nanoparticles dispersed in \(N,N,N\)-trimethyl-\(N\)-propylammonium bis(trifluoromethanesulfonyl)amide (N\textsubscript{1113}TFSA) with a mean diameter of 2.3 nm by the RTIL-sputtering method. The concentration of Pt nanoparticles in the RTIL increased with an increase in sputtering time; however, the mean particle size was almost constant. The obtained Pt nanoparticles could be easily immobilized on a glassy carbon electrode (GCE) by heating in the temperature range of 473–573 K. The Pt nanoparticle-immobilized GCE exhibited a clear cathodic current for ORR in an \(O_2\)-saturated 0.5 M (M = mol dm\textsuperscript{-3}) \(H_2SO_4\) aqueous solution, which indicated that the Pt nanoparticles prepared by the RTIL-sputtering method worked well as an ORR catalyst.\textsuperscript{31} Furthermore, we prepared
a composite of single-walled carbon nanotube (SWCNT) with Pt nanoparticles in RTILs by the sputtering method. CNTs are a promising supporting material for catalytically active metal nanoparticles owing to their large surface area and excellent physicochemical properties; however, the immobilization of metal nanoparticles on the chemically inert surface of CNTs is difficult without surface oxidation or surface modification with polymer coating. Interestingly, we found that the Pt nanoparticles prepared in \( N_{1113} \)TFSA by the sputtering method could be easily immobilized on untreated SWCNTs simply by agitating at 373 K. The loading amount of Pt nanoparticles on SWCNTs could be controlled by changing the concentration of Pt nanoparticles in the RTIL (the mean particle size was constant at 3.2–3.5 nm; Fig. 1). The nanoparticles could be immobilized on SWCNTs using ammonium-based RTILs, but not imidazolium-based RTILs such as 1-ethyl-3-methylimidazolium (EMI) TFSA. We analyzed the Pt-SWCNT composite by X-ray photoelectron spectroscopy (XPS) to understand the driving force for the immobilization of the metal nanoparticles on the sp\(^2\) carbon nanomaterial. The result suggested that the RTIL serves as a nanoglue between the Pt nanoparticles and the SWCNTs. In addition, we examined the electrocatalytic activity of the Pt-SWCNT composite for the ORR using the rotating ring-disk electrode technique and found that the Pt-SWCNT composite has great potential as an electrocatalyst for PEFCs. Further, we performed the accelerated degradation test on the composite by sweeping the potential between 1.0 V and 1.5 V vs. RHE, which is the potential range for the accelerated corrosion of carbon. As determined from the change in mass activity and electrochemical surface area (ECSA), interestingly, the durability of both the SWCNTs and the Pt-
immobilized carbon materials (Pt-Vulcan®) fabricated using the RTIL-sputtering method were higher than that of a commercially available catalyst (TEC10V30E) and the Pt-SWCNT composite prepared by the conventional method (Pt-SWCNTconv) (Fig. 2). In situ SEM/STEM analysis revealed the suppression of carbon corrosion, which suggests that the RTIL present between the Pt nanoparticles and carbon material prevented their reaction. Thus, the RTIL-sputtering method can easily produce highly durable catalysts, which can only be achieved using RTILs. Recently, Tsuda and Kuwabata et al. fabricated highly durable catalysts using RTILs and investigated the role of RTILs in catalyst synthesis. Thus, we hope to see innovative materials tailored by the RTIL-sputtering method.

2.2 Electrodeposition of metals from RTILs

The wide electrochemical potential window, which is one of the attractive features of RTILs, allows the electrodeposition (or electroplating) of many metals from RTILs by preventing hydrogen generation and the associated hydrogen embrittlement of metals that occur in aqueous electrolytes. The electrochemical potential window strongly depends on the structure of the RTILs, and the cathodic and anodic limits are often dominated by the structure of the cation and anion, respectively. Thus, various combinations of RTILs and precursor metal salts have been extensively investigated. The present section briefly introduces our research on the electrodeposition of some metals using RTILs as electrolytes.

We investigated the electrodeposition of various metals and the electrochemical behaviors of metal
ions using RTILs composed of aliphatic cations and TFSA anion, which have a high reduction stability and relatively low viscosity.\textsuperscript{42-53} Pd and Pt are two of the important metals used in scientific and industrial fields owing to their good physical and chemical properties such as corrosion and wear resistance. Therefore, the electrodeposition of Pd and Pt from RTILs has been extensively investigated; however, the precursor metal salts were limited to halogeno complexes.\textsuperscript{54,55} To reduce the halogen contamination of the deposits, we investigated the electrodeposition of Pd and Pt from acetylacetonate (acac) complexes used as precursors.\textsuperscript{42,46,49} The cyclic voltammograms of a GCE in 1-butyl-1-methylpyrrolidinium TFSA (Pyr\textsubscript{1,4}TFSA) without and with 5 mM Pd(acac)\textsubscript{2} at room temperature are shown in Fig. 3. Two cathodic peaks appeared at $-2.0$ V and $-2.4$ V vs. Ag$|$Ag(I). To examine the reduction peak at $-2.0$ V, potentiostatic cathodic reduction was conducted at $-2.0$ V on the GCE. A shiny black deposit formed on the GCE, which was confirmed to be Pd(0) by SEM-EDX analysis and XPS. To further clarify the electrochemical reaction at $-2.0$ V, RRDE analysis was performed, which led to the generation of a reduction current at the disk electrode and an oxidation current at the ring electrode held at $-1.25$ V.\textsuperscript{56} The current at the ring electrode was considered to generate from the oxidation reaction of [Pd(acac)\textsubscript{2}]\textsuperscript{-}; this suggests that the reduction of Pd(acac)\textsubscript{2} to Pd(0) proceeded as a disproportionation reaction via the formation of [Pd(acac)\textsubscript{2}]\textsuperscript{2-}. Metallic Pt was also obtained from Pt(acac)\textsubscript{2} in Pyr\textsubscript{1,4}TFSA and $N,N,N$-triethyl-$N$-methylammonium TFSA (N\textsubscript{1666}TFSA).\textsuperscript{46,49} The results indicate that acac complexes are useful non-halogenated precursors for the electrodeposition of Pd and Pt.
As mentioned in the previous section, monodisperse metal nanoparticles can be obtained in RTILs without using stabilizers. Katayama et al. prepared metal nanoparticles in RTILs by the electrochemical method.\textsuperscript{57} When a potential sufficiently lower than the point of zero charge of RTILs is applied to RTILs containing metal ions, the deposition of metals on the electrode is inhibited by the accumulation of the cations on the electrode; consequently, the reduced metals disperse in the RTILs as nanoparticles.\textsuperscript{58,59} Moreover, Pd and Pt nanoparticles were formed in RTILs containing Pd(acac)\textsubscript{2} and Pt(acac)\textsubscript{2}, respectively, via galvanostatic deposition as determined by TEM analysis (Fig. 3).\textsuperscript{42,46,49} Pd nanoparticles were prepared in RTILs with different alkyl side chain lengths, and it was found that the mean particle size slightly decreased when ionic liquids with longer alkyl side chains were used.\textsuperscript{43} Further, the rotating electrode method was used to investigate the effects of rotation speed and applied potential on the particle size of Pt nanoparticles; however, these factors were found not to affect the particle size.\textsuperscript{49} Furthermore, we prepared Cd and Se nanoparticles by a similar electrochemical reduction method.\textsuperscript{44,52} Although we have prepared metal nanoparticles in RTILs by the RTIL-sputtering and electrochemical reduction methods, we have not yet established a method to obtain the desired particle size. We expect that future research will elucidate the correlation between the structure and physicochemical properties of RTILs and the particle size of metal nanoparticles, and the application scope of metal nanoparticles stabilized in RTILs will further expand.

Since the electrodeposition of Al from aqueous solutions is hindered by hydrogen evolution, a plating bath of nonaqueous solvents is required. The application of RTILs to the Al electroplating technology
has a long history, and AlCl$_3$- and AlBr$_3$-based RTILs have been widely used for investigating the electrodeposition of Al and Al alloys.$^{60}$ Haloaluminate-based RTILs have attracted considerable attention as an electrolyte for Al-ion batteries owing to their high ionic conductivity and high current efficiency.$^{61,62}$ We developed a polymer gel electrolyte using AlCl$_3$-based RTILs and investigated the electrochemical behavior of Al species in TFSA$^-$-based RTILs.$^{63,64}$ The electroactive species of the RTILs are Al-containing anions such as Al$_2$Cl$_7^-$ and Al$_2$Br$_7^-$.

Since the anionic species move against the electric field under reducing conditions, which may cause polarization and decrease the current efficiency, RTILs with Al-containing electroactive cationic species need to be developed. In this context, we developed a new RTIL via the complexation of AlCl$_3$ and 4-propylpyridine (4-Pr-Py) as a neutral ligand.$^{65}$ We found that the addition of excess AlCl$_3$ to 4-Pr-Py led to the formation of [AlCl$_2$(4-Pr-Py)$_2$]$^+$, which was the electroactive species for the electrodeposition of Al. The formation of cationic species improved the thermal stability, and the evaporation temperature of the mixture (ca. 523–543 K) was higher than the evaporation temperatures of AlCl$_3$ and 4-Pr-Py (433 K and 368 K, respectively) (Fig. 4). In addition, we found that the RTIL composed of AlCl$_3$ and 4-Pr-Py were much more stable against exposure to air than the classical haloaluminate-based RTILs. In recent years, various Al-based RTILs have been reported and are increasingly applied to not only plating but also energy devices. Since the electrodeposition of Al is possible only with RTILs, further advancement is expected in the research and development in this field.
3. Design, Synthesis, and Structure-Physicochemical Property Relationship of RTILs

One of the attractive features of RTILs is the tenability of their physicochemical properties by varying the combination of cation and anion. A large number of RTILs have been reported so far, and the correlation between the structure and physicochemical properties of RTILs has been extensively studied. The synthesis of novel RTILs and elucidation of their structure-physicochemical property relationship are important as they can provide design guidelines for ionic liquids with desired properties and functions. Considering this, we designed and synthesized tri-n-butylalkylphosphonium cation- and aryltrifluoroborate anion-based RTILs and investigated their structure-physicochemical property relationship.\(^{66-68}\) Although the structure-physicochemical property relationship of anion-based RTILs using structural isomers has not been studied so far, by using aryltrifluoroborate anions, we were able to clarify the effect of the position of the substituent on the benzene ring on the physicochemical properties of the RTILs. Currently, we are researching RTILs with ether oxygen atoms in the side chain. Although the introduction of ether oxygen atoms into the side chain of RTILs has been reported to decrease the viscosity and increase the ionic conductivity of the RTILs compared with those of RTILs with alkyl analogs in the side chain, the effects of the position and number of ether oxygen atom in the side chain on the physicochemical properties of the RTILs remain unclear.\(^{69}\) We prepared various ether-functionalized pyrrolidinium-based RTILs and carefully analyzed them by comparing their physicochemical properties with those obtained by Ab initio quantum mechanics calculations and molecular dynamics (MD) simulations.\(^{70,71}\) The results confirmed that the introduction
of ether oxygen atoms at a position close to the pyrrolidinium ring yields RTILs with low viscosities (Fig. 5). Furthermore, MD simulations revealed that the transport properties was improved by disturbing the ion arrangement. It is hoped that the combination of computational and experimental chemistry will lead to further progress in the study of the structure-property relationships of RTILs.

4. Secondary Batteries Using Nonaqueous Electrolytes

4.1 RTILs as electrolytes for secondary batteries

From safety perspective, RTILs can be excellent electrolytes for batteries owing to their non-volatility and non-flammability. Since the publication of the pioneering paper describing the reversible intercalation and deintercalation of lithium ions into a graphite electrode in a bis(fluorosulfonyl)amide (FSA) anion-based RTIL,\textsuperscript{72,73} the application of RTILs as electrolytes in lithium-ion batteries has been extensively researched.\textsuperscript{12,14} Moreover, owing to the increasing demand for batteries with high energy densities, lithium metal negative electrodes having a high theoretical energy density and low redox potential have been actively studied. We have been investigating the deposition and dissolution of metallic lithium using pyrrolidinium-based RTILs and solvated ionic liquids as electrolytes.\textsuperscript{74,75} For example, we have shown that the use of lithium phosphorus oxynitride as an artificial solid electrolyte interphase on an electrode suppresses the reductive decomposition of the electrolyte and increases the Coulombic efficiency of the deposition and dissolution of metallic lithium in RTILs.

In recent years, potassium secondary batteries have attracted considerable attention owing to the
abundance of potassium resources and the higher voltage and comparable theoretical energy density of potassium secondary batteries compared with those of lithium-ion batteries. Another advantage of potassium secondary batteries is that the intercalation reaction with graphite can be used as the negative electrode reaction. We have reported that potassium-containing composite oxides (K_{2}M_{2}TeO_{6}) with a honeycomb layered structure can be used as positive electrode materials, which exhibit charge and discharge at approximately 4 V, and have found that pyrroldinium-based RTILs are suitable as electrolytes. We evaluated the physicochemical properties of 1-methyl-1-propylpyrrolidinium TFSA (Pyr_{1,3}TFSA) containing 0.5 M KTFSA (0.5 M KTFSA/Pyr_{1,3}TFSA) and found that its viscosity and ionic conductivity are respectively lower and higher than those of 0.5 M LiTFSA/Pyr_{1,3}TFSA and 0.5 M NaTFSA/Pyr_{1,3}TFSA. The weak Lewis acidity of the K ion might be the cause of the high ionic conductivity of the electrolyte. Further, we measured the electrochemical potential window of the RTILs by voltammetry using Ni and Pt working electrode to measure the cathodic and anodic limit, respectively (Fig. 6). The anodic limits of the three RTILs were almost the same; however, the deposition and dissolution potential of 0.5 M KTFSA/Pyr_{1,3}TFSA was the lowest among the three RTILs. This result is consistent with the findings of previous studies on the reduction potential of alkali metal ions in other types of RTILs. Further, we found that the potassium symmetric cell assembled with 0.5 M KTFSA/Pyr_{1,3}TFSA performed stably, as determined by galvanostatic deposition and dissolution of potassium at 298 K. When K_{2}Ni_{0.75}Co_{0.25}TeO_{6} was used as the positive electrode, charge and discharge occurred at an average voltage of ca. 3.7 V and the capacity retention rate was
approximately 80% even after 100 cycles. Although the obtained capacity (only a few tens of mAh/g) is not as high as those of the cathode materials currently used for lithium-ion batteries, we expect to realize a potassium-ion battery system with a high capacity using RTILs by nanosizing the electrode material and optimizing the components.

4.2 Secondary batteries with lithium metal negative electrode using organic electrolytes

With the increasing demand for high-energy density secondary batteries, metallic lithium has become popular as a negative electrode owing to its high theoretical capacity and low redox potential. However, the practical implementation of metallic lithium as a negative electrode is hindered by several issues, including inhomogeneous deposition, large volume change, and poor safety. Inhomogeneous deposition leads to a low Coulombic efficiency during charge-discharge cycling.\(^{81,82}\) Previous studies have shown that the formation of a surface film during the early stages of deposition may affect the deposition morphology. Lithium fluoride (LiF) is one of the main components of this surface film and is considered to play an important role in the subsequent metallic lithium deposition.\(^{83,84}\) Therefore, we investigated the electrodeposition of lithium using 1.0 M LiPF\(_6\)/propylene carbonate (PC) with and without trace amounts of water to control the surface film formed during deposition.\(^{85}\) We measured the change in the water content of the electrolyte containing a trace amount of water (100 or 1000 ppm) and found that the water content decreased with time; this indicated that LiPF\(_6\) reacted with water and decomposed to form HF and H\(_3\)PO\(_4\). Fig. 7 shows the digital photographs and SEM images of the Cu
electrode with electrodeposited lithium. The SEM images of the samples prepared without water or on day 1 after the addition of 100 ppm water show similar inhomogeneous deposition under both the conditions, which indicates that the addition of water initially had little effect on the morphology of the deposited lithium. In contrast, noticeable change was observed in the deposit (blue coloration) on day 2 and the formation spherical deposits as confirmed by SEM. The cross-sectional FE-SEM images of the deposited lithium show densely packed columnar lithium structures. In the case of electrolyte with 1000 ppm water, the sample prepared on day 1 appears gray with large granular deposits on top of small granular deposits as confirmed by SEM. However, the sample prepared on day 2 exhibit a thin white deposit on the Cu substrate after electrodeposition, where there was no metallic lithium on the electrode. Since we thought that the film formed before deposition played an important role in determining the morphology of the deposits, we analyzed the samples by XPS, Auger electron spectroscopy (AES), and reflection electron energy loss spectroscopy (REELS), electrochemical quartz crystal microbalance (EQCM) technique, and hard X-ray photoelectron spectroscopy (HAXPES) using a synchrotron. The results revealed that in the regions with the densely packed columnar lithium deposits, a LiF-rich film of approximately 10.0 µg cm$^{-2}$ was formed prior to the deposition of lithium. In contrast, in the electrolyte with 1000 ppm water, the thickly deposited LiF inhibited the deposition of metallic lithium. Although previous studies reported that LiF-rich films have a positive effect on the morphology of the deposited lithium, we found that the film should contain an appropriate amount of LiF. Although the composition and role of the film remain unclear, future
research is expected to provide a better understanding of the deposition of lithium.

To construct batteries with high energy densities using metallic lithium as the negative electrode, thin metallic lithium must be used at high utilization. However, limited information is currently available on the effects of lithium utilization on the cycle performance of cells.\(^{86-88}\) Thus, we performed charge/discharge tests using cells composed of \(\text{LiFePO}_4\) (LFP) and metallic lithium at various lithium utilization values.\(^{89}\) The electrolyte used was 1.0 M LiTFSA in EC:PC (1:1 vol%). The capacity of the cell with 1% lithium utilization degraded negligibly after 300 cycles even when 50 \(\mu\)m metallic lithium was used, whereas the capacity of the cells with 5, 11, 16, and 30% lithium utilization rapidly decayed after approximately 250, 150, 100, and 30 cycles, respectively. Further, we added typical additives, fluoroethylene carbonate (FEC) and vinylene carbonate (VC), to the electrolyte at a lithium utilization of 30%. Fig. 8 shows the discharge capacity and charge/discharge curves of the cell using the electrolyte with FEC and VC. The cycle characteristics of both the additives depended on their amounts; however, capacity decay was hardly observed after 100 cycles with the addition of 5 wt% in FEC. The cross-sectional FE-SEM images of the electrodes after charge/discharge cycles showed that the electrolyte with FEC had less deposit and lower metallic lithium consumption compared with the electrolyte without FEC. This suggests that the decomposition of the electrolyte was suppressed by the film formed on lithium after the addition of FEC. Thus, for the practical application of metallic lithium, not only utilization rate and additives, but also other parameters such as separator, confined pressure, cell shape, and electrolyte volume need to be considered. We hope that our experimental results will
provide important insights for future research in this field.

5. Conclusion

We present a comprehensive review of our research on the electrodeposition of metals and preparation of metal nanoparticles in nonaqueous electrolytes and their application to energy devices. The Pt nanoparticles prepared using RTILs as the reaction media exhibit better durability against ORR compared with commercial electrocatalysts. Moreover, various metals can be deposited by designing the electrolyte. In addition, we studied the deposition, morphology, and lithium utilization of metallic lithium, which is used as a negative electrode in next-generation batteries with high energy densities. The findings presented here will lead to further progress in materials synthesis and energy devices using nonaqueous electrolytes. In recent years, research on energy devices using solid electrolytes has progressed at a rapid pace and their practical application is highly expected; however, solution-based energy devices will continue to evolve and occupy the market. We hope that the synthesis of materials using nonaqueous electrolytes as reaction media, the design of new electrolytes, and innovative devices utilizing these will continue to emerge.

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**Figure Caption**

**Figure 1.** TEM images of Pt nanoparticle–SWCNT composite fabricated by RTIL-sputtering method. The RTIL used was (a–c) N1113TFSA and (d) EMITFSA. The sputtering time was (a) 300 s, (b) 600 s, and (c, d) 900 s. Reproduced by permission of The Royal Society of Chemistry. 32

**Figure 2.** Variation in a) ECSA and b) catalytic activity retention rate for ECSA as a function of cycle number. The electrocatalysts were ●) Pt-SWCNT, ○) Pt-SWCNTconv, ■) Pt-Vulcan®, and ▲) TEC10V30E. Reproduced with permission from Ref. 33.

**Figure 3.** (a) Cyclic voltammograms of a GCE in (—) BMPTFSA and BMPTFSA containing 5 mM Pd(acac)2 reversed at (—) −2.1 V and (—) −2.6 V. The temperature was 25 °C, and the scan rate was 50 mV s\(^{-1}\). (b) SEM image of the deposit on the GCE and (c) EM images of Pd nanoparticles formed by potentiostatic electrodeposition at −2.0 V. Electric charge was 2.4 C. Reproduced with permission from Ref. 42.

**Figure 4.** Thermogravimetric analysis curves of AlCl3, 4-propylpyridine, and their complexes at different ratios measured under an inert atmosphere of helium at a heating rate of 20 °C/min. Reproduced with permission from Ref. 65.

**Figure 5.** Temperature dependence of (a) viscosity and (b) ionic conductivity of RTILs: (red○) Pyr1,3TFSA, (red●) Pyr1,4TFSA, (blue◇) Pyr1,1O1TFSA, (blue◆) Pyr1,1O2TFSA, and (green■) Pyr1,2O1TFSA (Pyr1,3\(^{+}\) = 1-methyl-1-propylpyrrolidinium, Pyr1,4\(^{+}\) = 1-butyl-1-methylpyrrolidinium, Pyr1,1O1\(^{+}\) = 1-methoxymethyl-1-methylpyrrolidinium, Pyr1,1O2\(^{+}\) = 1-ethoxymethyl-1-methylpyrrolidinium, and Pyr1,2O1\(^{+}\) = 1-ethoxyethyl-1-methylpyrrolidinium). Reproduced with permission from Ref. 70.

**Figure 6.** Electrochemical stability of TFSA-based ionic liquids containing alkali metal ion at 298 K. Voltammograms of 0.5 M KTFSA/Pyr1,3TFSA, 0.5 M LiTFSA/Pyr1,3TFSA, and 0.5 M NaTFSA/Pyr1,3TFSA at 298 K. The potential is shown using ferrocene (Fc/Fc\(^{+}\)) as a reference. The working electrodes were Ni (cathodic limit) and Pt (anodic limit), respectively. Scan rate was 1 mV s\(^{-1}\). Reproduced from Ref. 77.

**Figure 7.** Digital photographs and SEM images of the deposit produced in 1.0 M LiPF6/PC (a, f) without water and with (b, g) 100 ppm water (day 1), (c, h) 100 ppm water (day 2), (d, f) 1000 ppm water (day 1), and (e, j) 1000 ppm water (day 2). Applied current and charge were 0.1 mA cm\(^{-2}\) and...
0.5 mAh cm\(^{-2}\), respectively. Reproduced with permission from Ref. 83.

**Figure 8.** Discharge capacity vs. cycle number and charge/discharge curves of a LFP/Li cell. The electrolyte was 1.0 M LiTFSA in EC:PC (1:1 vol%) containing (a, b) FEC and (c, d) VC. The charge/discharge test was performed at 0.2C rate at 25 °C. Reproduced from Ref. 87.
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