## Special Review

# Serendipitous Discoveries in Studies of Electrolytes, Conjugated Materials and Molecular Complexes

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■**ABSTRACT**‖ During my first 15 years at Toyota Central R&D Labs, Inc. (Toyota CRDL), I studied the stimulus-response properties of ionic gels and soluble conjugated polymers, whereas the second half of my career was focused on leading-edge battery technology. This work involved attempts to improve upon Li-ion batteries using catalytic cycles based on adding coordination complexes to electrolytes. In many cases, my work ranged from confirmatory studies to evaluation of the actual properties or behavior of processes that had been developed. During this work, I encountered various unexpected and yet fortuitous results. Here, I introduce five examples of such serendipitous discoveries made during research regarding the physical chemistry of specific materials, and describe engineering applications associated with these discoveries.

## 1. Introduction

More than 40 years have passed since I first joined Toyota Central R&D Labs, Inc. (Toyota CRDL). In the first half of my career at Toyota CRDL, I worked to develop polymeric materials such as polyelectrolyte gels and conjugated polymers because I had majored in polymer chemistry at Kyoto University. This changed in 1994, when I joined a Li-ion battery program and began to research advanced battery materials, especially electrolytes and additives. I have worked in this field from that point up to the present. During this time, I was fortunate to discover various novel physicochemical phenomena while researching electrolytes, conjugated materials and molecular complexes, and was able to develop engineering applications for these phenomena.

By definition, electrolytes are substances that produce an electrically-conductive solution when dissolved in a polar solvent such as water. This occurs because, once dissolved, an electrolyte separates into cations and anions (**Fig. 1**(a)) that subsequently disperse uniformly throughout the solvent. A conjugated molecule is one that incorporates a system of alternating double and single bonds between carbon atoms in which the electrons in p orbitals are delocalized, such that the overall energy of the molecule is lowered and
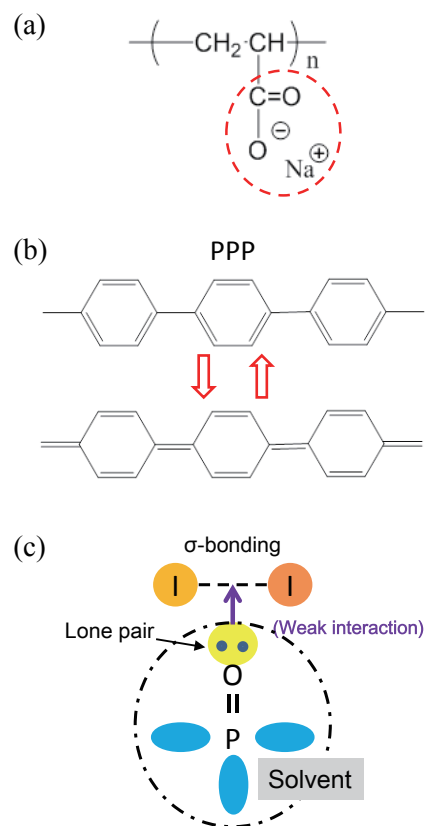


**Fig. 1** Examples of (a) a polymeric electrolyte, (b) a conjugated structure, and (c) a molecular complex between iodine and a solvent.

its stability increased. Figure 1(b) shows an example of a conjugated polymer incorporating phenyl units. Molecular complexes comprise a central atom or ion, termed the coordination center, and a surrounding array of bound molecules or ions, known as ligands or complexing agents. These complexes are formed as a result of relatively weak interactions between electron donors and acceptors (Fig. 1(c)).

In this paper, I introduce five serendipitous discoveries that resulted from my research work at Toyota CRDL. The first is the discovery of the bending motion of polyelectrolyte gels in aqueous solutions in response to an electric field, which was employed to design soft, flexible actuators. The second is an electrorheological effect exhibited by silicone gels that permits the active control of sounds and vibrations via the application of electric fields. Thirdly, our research group determined that the time-resolved fluorescence of soluble conjugated polymers is affected by stress. Using this property, we succeeded in monitoring stress in automobile components. The fourth discovery was the chemical decomposition of magnesium oxide (MgO) by iodine species in specific solvents. This phenomenon was applied to produce a catalyst for use in rechargeable $Mg-O_2$ batteries providing high specific energy densities. Finally, we discovered the anomalously high redox potential of iodine species, which was used to realize lithium recovery from de-activated lithium materials.

## 2. Discovery of New Phenomena

### 2. 1　Bending of Polyelectrolyte Gels in Electric Fields

Polyacrylamide (PAAm) is a typical water-soluble polymer prepared by the radical polymerization of acrylamide. When bis(acrylamide) is introduced as a cross-linker during the polymerization process, a crosslinked polymer is obtained that will form a polyelectrolyte gel in an aqueous NaOH solution. The amide groups ($CONH_2$) in PAAm can be hydrolyzed to produce COONa units that will dissociate into $Na^+$ and $COO^-$ ions (Fig. 1(a)). As a consequence, the polymer will swell in water to increase its volume by several orders of magnitude and form a polyelectrolyte gel. These gels are unique materials in which a solid and liquid coexist, and they undergo swelling and shrinking in response to changes in environmental parameters such as pH, solvent composition and temperature. As

the demand for soft, flexible actuators increased in the early 1980s, we began to study the electric field response of polyelectrolyte gels. The characteristics of PAANa gels in response to electric fields was first reported by Hamlen et al. in 1965.[1] In this work, gel fibers in contact with anodes in aqueous NaCl solutions were observed to shrink when a dc electric field was applied (**Fig. 2**(a)). In 1982, Tanaka et al. reported a phase transition with an accompanying volume change for a gel not in contact with an anode, in an acetone/water solution. The application of a 2 V dc electric field induced shrinkage of the gel (Fig. 2(b)).[2] In our own trials, a PAANa gel in an aqueous $Na_2CO_3$ solution that was not in contact with the anode also exhibited partial swelling deformation at the anode side following the application of a 10 V electric field (Fig. 2(c)).[3] In addition, a bar-shaped PAANa gel could be induced to bend towards the cathode side based on the bimetal principle in response to a dc voltage (Fig. 2(d)). Switching the polarity of the voltage caused the bent gel to shrink at the anode
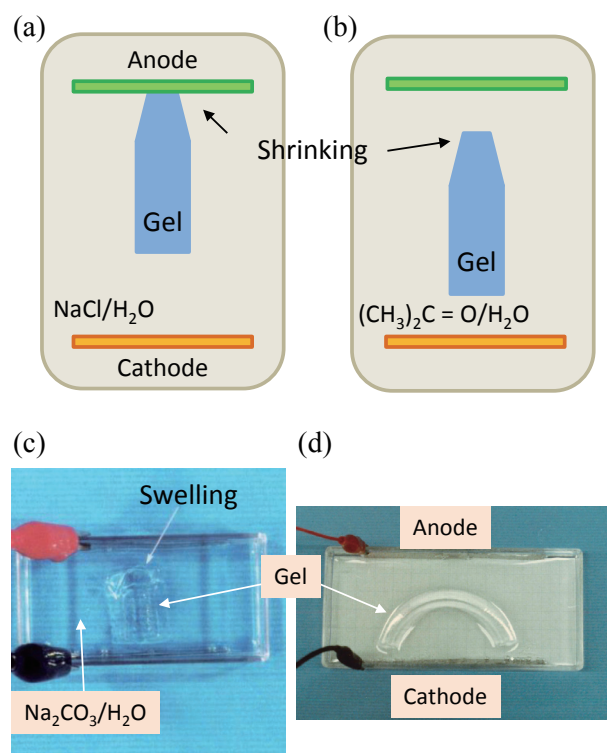


**Fig. 2**　Deformation of polyelectrolyte gels in dc electric fields: (a) shrinking of gel in contact with anode, (b) shrinking of gel not in contact with anode, and (c) swelling and (d) bending of gel not in contact with anode.

side and straightened again. The partial swelling of the gel was attributed to changes in osmotic pressure resulting from the different mobile ion concentrations inside and outside the gel.[4,5]

This bending of a polyelectrolyte gel in response to an electric field represented a novel phenomenon and was selected as a national project with the aim of developing biomimetic actuators using stimuli-responsive gels. This project was pursued for six years, during which time a suitably tough gel that were highly responsive to electric fields was researched and developed. This material comprised a physically crosslinked gel prepared by freezing/melting of an aqueous solution of poly(vinyl alcohol) and poly(sodium acrylate) (that is, a PVA-PAA gel). Based on this material, we designed two gel actuators prototypes: robotic hands with PVA-PAA gel fingers and artificial fish with PVA-PAA gel tails.[6]

## 2. 2 Electrorheological Behavior of a Particle Composite Gel

Suspensions made of polymer particles having high dielectric constants dispersed in non-conducting oils will stiffen rapidly when subjected to electric fields on the order of 1 kV/mm. This rheological behavior, known as the electrorheological (ER) effect, was first reported by Winslow in 1947. This effect appears when dispersed particles are polarized upon the application of an electric field. These electrically polarized particles subsequently move and align between the electrodes, such that the numerous polymeric chains form a crosslinked polymer network and the viscosity is increased.[7-9] One challenge associated with the ER effect is sedimentation of particles dispersed in oil over prolonged time spans. This occurs due to the different specific gravities of the particles and oil. To address this phenomenon, we proposed using a gel instead of oil. This concept was inspired by the work of a fellow researcher in the same laboratory who was studying gas adsorption by water-insoluble gels. Our work showed that, if a crosslinked network of particles is formed in advance, the ER effect can also be obtained in a gel (**Figs. 3**(a) and (b)). That is, we were able to create a new material (which we termed an ER gel), the modulus of which could be tuned by applying an electric field.[10] This material was expected to have applications as a shock absorber to actively reduce sounds and vibration. Figure 3(c)

shows the storage modulus values for ER gels made of dispersed particles of poly-p-phenylene (PPP)[11] and poly(3-hexylthiophene) (P3HT) in silicone under a dc electric field. Although the storage modulus for the PPP ER gel increased with increasing electric field intensity, the P3HT-ER gel exhibited a decreased modulus in response to an electric field of more than 1.5 kV/mm.[12] In addition, we unexpectedly observed
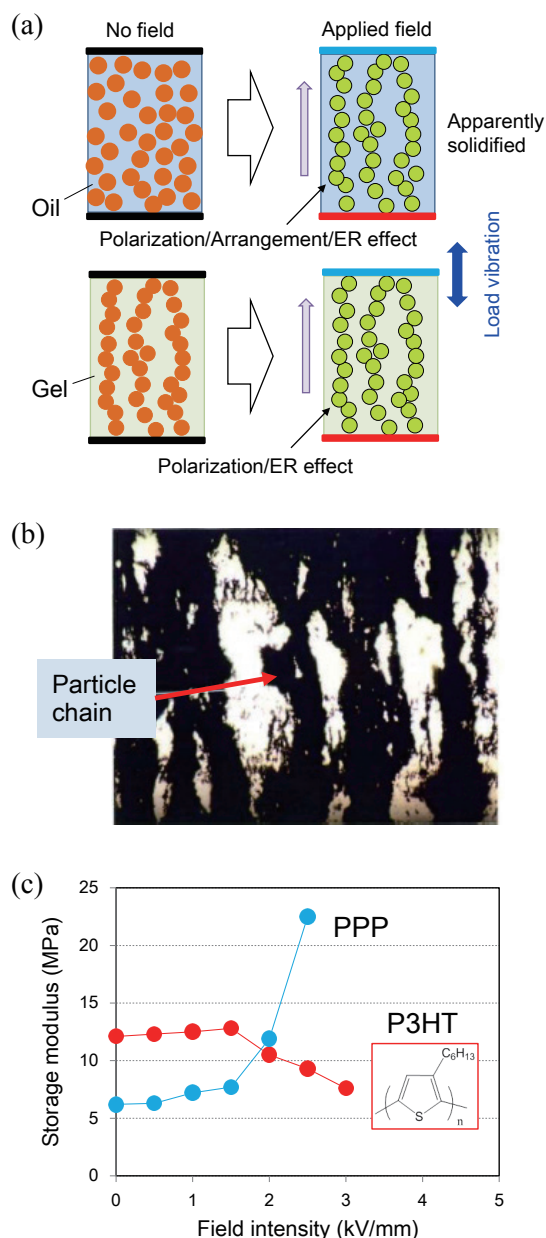


**Fig. 3** (a) Schematic illustration of ER effect in conjugated polymer composite gel, (b) micrograph of chains within poly-*p*-phenylene (PPP) particles in gel, and (c) electro-rheological effect as exhibited by silicone gels containing PPP or P3HT particles.

an electroplastic effect in this gel, because the glass transition temperature of the P3HT was close to ambient temperature.

These ER gels are interesting composites in that it is possible to actively control their modulus by the application of an electric field. Therefore, these materials can be used for attenuation of sounds and vibrations. The use of ER gels consisting of polymer particles with high dielectric constants and non-conducting gels also allows a significant variety of materials to be designed. As an example, if magnetic particles such as Fe/Co/Ni alloys and ferrites are used, magneto-rheological behavior may be observed. We have already designed magnetic field-responsive composites incorporating iron particles.[13]

## 2. 3 Time-resolved Fluorescence from P3OT in Polymer Films under Stress Loading

In the early 1990's, Hamamatsu Photonics K. K. developed a time-resolved fluorescence instrument with a pen-type probe that allowed the fluorescence of various specimens to be assessed regardless of the sample morphology. In this technique, the sample is excited by a light pulse having a pulse width on the order of picoseconds and subsequently emits fluorescent light, the intensity of which decays with time (**Fig. 4**(a)). The fluorescence lifetime, $\tau$, is calculated using the equation

$$I = \Sigma A_i \exp(-t/\tau_i), \tag{1}$$

where $I$ is the intensity of the fluorescent emission, $A_i$ is a constant, $t$ is time and $\tau$ is the emission lifetime.

Poly(3-alkylthiophene) (P3AT) analogues having long side chains, such as $C_4H_9$, $C_6H_{13}$, and $C_8H_{17}$, are typical conjugated polymers that exhibit good solubility in organic solvents and show UV-Vis absorption spectrum changes.[14-16] We studied the time-resolved fluorescence generated by P3AT dispersed in a poly(methyl methacrylate) (PMMA) film under tensile loading (Fig. 4(b)).[17] The PMMA film matrix used in this work showed elastic deformation in response to applied strains below 0.5%. In these trials, the PMMA films contained 0.2% poly(3-octylthiophene) (P3OT), using P3OT samples having various molecular weights, and the effect of applied tensile stress on the time-resolved fluorescence lifetime of the P3OT was examined. As shown in

Fig. 4(c), the fluorescence lifetime of P3OT samples with larger molecular weights decreased linearly as the tensile loading was increased.[18]

Many different polymeric coatings are applied to the steel substrates used in automobile assemblies, and are subjected to internal or residual stresses during curing. Internal stress in particular can induce fractures and
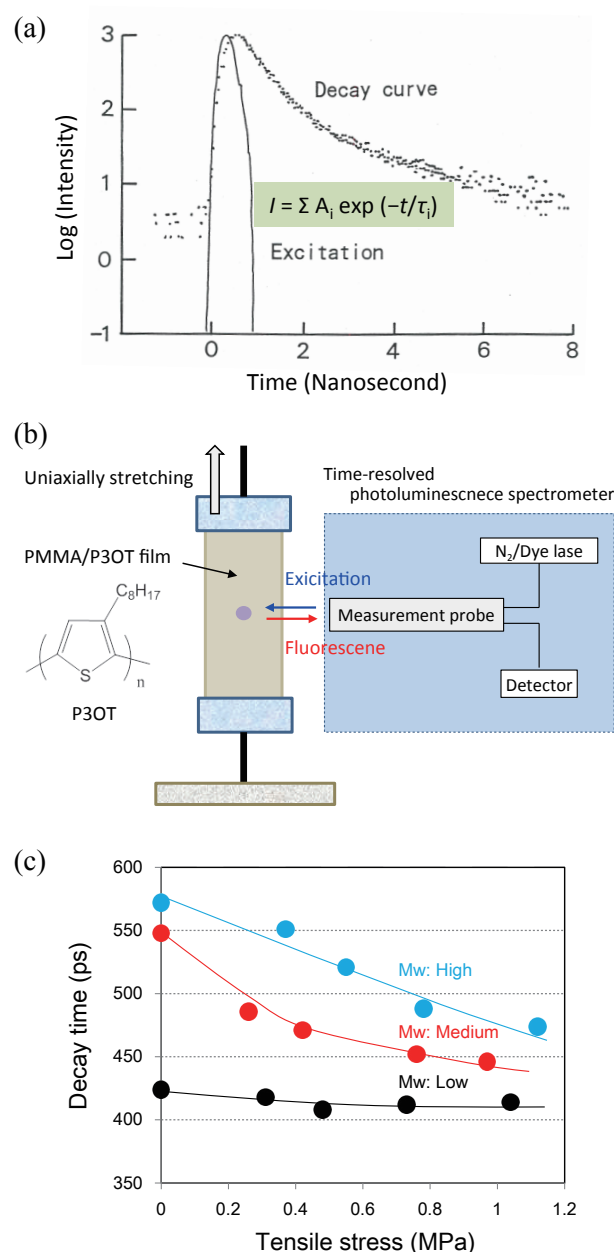


**Fig. 4** (a) Typical time-resolved fluorescence decay curve, (b) schematic illustration of instrumentation used to analyze time-resolved fluorescence of P3OT in PMMA under stress loading, and (c) fluorescence lifetime of P3OT samples having different molecular weights as function of stress.

thus may greatly affect the reliability of polymeric coatings.[19] As an example, in work performed 25 years ago, cracks were observed in a melamine resin clear coating applied to metal substrates following accelerated weathering tests. Our group attempted to use the relationship between the fluorescence of P3OT and the stress described above to quantify the internal stress in the coatings. In this work, clear coatings containing 0.2% P3OT were sprayed onto metal substrates and cured. During curing, the coating attempts to shrink as the crosslinking reaction proceeds and, because the cured coating cannot slide on the substrate, two-dimensional tensile stress is generated. For the sake of simplification, we can assume that this two-dimensional stress is equal to the one-dimensional tensile stress produced when a free-standing polymer film incorporating P3OT is uniaxially stretched (**Fig. 5**(a)). In our work, we measured fluorescence lifetimes under various applied tensile stresses to create a calibration curve between fluorescence lifetime and tensile stress. Subsequently, this curve could be used to estimate internal stresses at various points on the metal substrate based on the measured fluorescence lifetime at those points. Figure 5(b) summarizes the internal stress distribution in the upper clear coating of a four-layer coating system on the door plate of an automobile, based on data obtained using P3OT with a molecular weight of 46700. The internal stress in the topcoat was on the order of 1 MPa, which is much less than the tensile stress at break for a free-standing coat (40 MPa).[20,21] The internal stress determined in this manner was also approximately equal to that obtained using the traditional thin film deflection method. This nondestructive technique for finding the internal stresses in coatings enables the stress distribution to be analyzed in various ways. As an example, the residual stress at the surface of injection-molded composite polymers has been investigated using 9-methylanthracene as a fluorescence label.[22]

## 2. 4  Observation of MgO Decomposition in an Iodine-DMSO Solution

Non-aqueous Li-air batteries[23,24] are secondary cells and can potentially provide energy levels of more than 1000 Wh/L. However, these devices have a serious problem in that large amounts of lithium peroxide ($Li_2O_2$) are precipitated at the cathode during discharge. Because $Li_2O_2$ is explosive, it is challenging to safely incorporate these batteries into vehicles. Mg-$O_2$ batteries can deliver the same energy levels and are also safe to operate because the inert compound magnesium oxide (MgO) is formed as a discharge product at the cathode. These batteries are therefore expected to be much less hazardous. Unfortunately, the discharge product (MgO) formed at the cathode cannot be decomposed by electrical charging at ambient temperatures; the non-aqueous Mg-$O_2$ battery may operate as a primary cell. A charging catalyst that accelerates the decomposition of MgO would be required to allow their use as secondary cells.

Iodine molecules are known to form 1:1 complexes with various organic solvents as a result of a charge-transfer interaction between functional groups in the solvent (the donor) and the σ bonds of
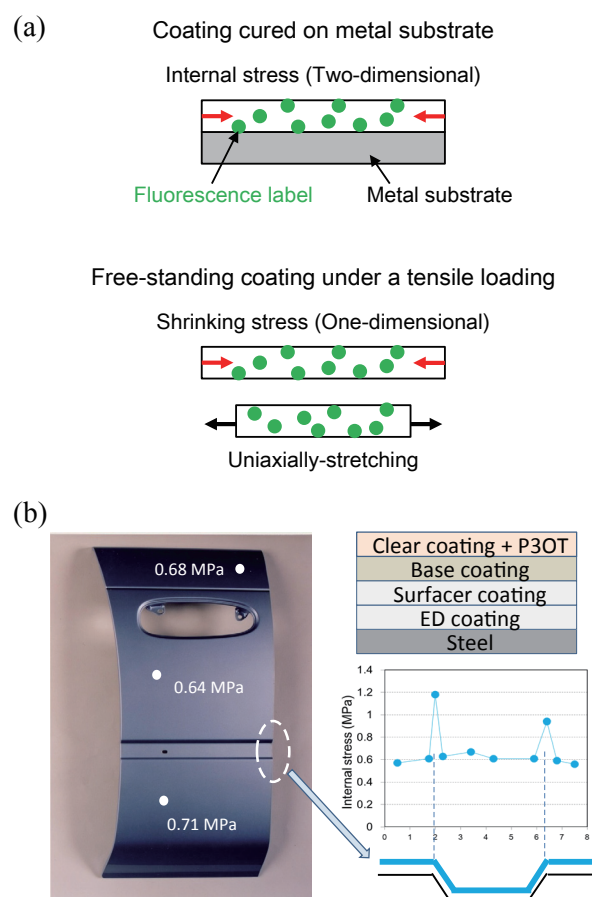


**Fig. 5**  (a) Shrinking stress in coating cured on metal substrate compared to internal stress in free-standing coating induced by uniaxially stretching and (b) internal stress distribution in clear coating on automobile body.

the iodine molecule (the acceptor).[25-27] As an example, a solution of iodine in dimethyl sulfoxide (DMSO) will show a yellow coloration due to strong complexion (**Fig. 6**(a)). By chance, I observed a slight loss of color in a DMSO solution containing iodine in which MgO powder was suspended during a storage test at 60°C.[28] Analysis of this solution suggested that



(a)

(b)



(c)
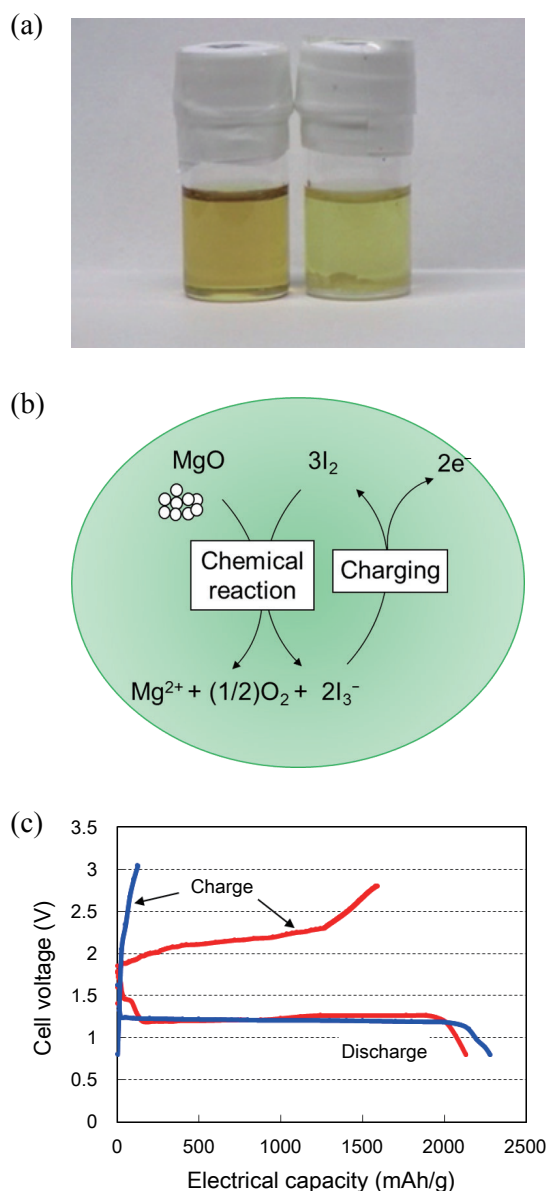


**Fig. 6**　(a) Photographic images of $I_2$-DMSO solutions without (left) and with (right) MgO after heating, (b) schematic illustration of catalytic cycle during MgO decomposition using iodine as mediator, and (c) first discharge/charge curves for Mg-$O_2$ batteries using DMSO electrolytes with (red) and without (blue) iodine.
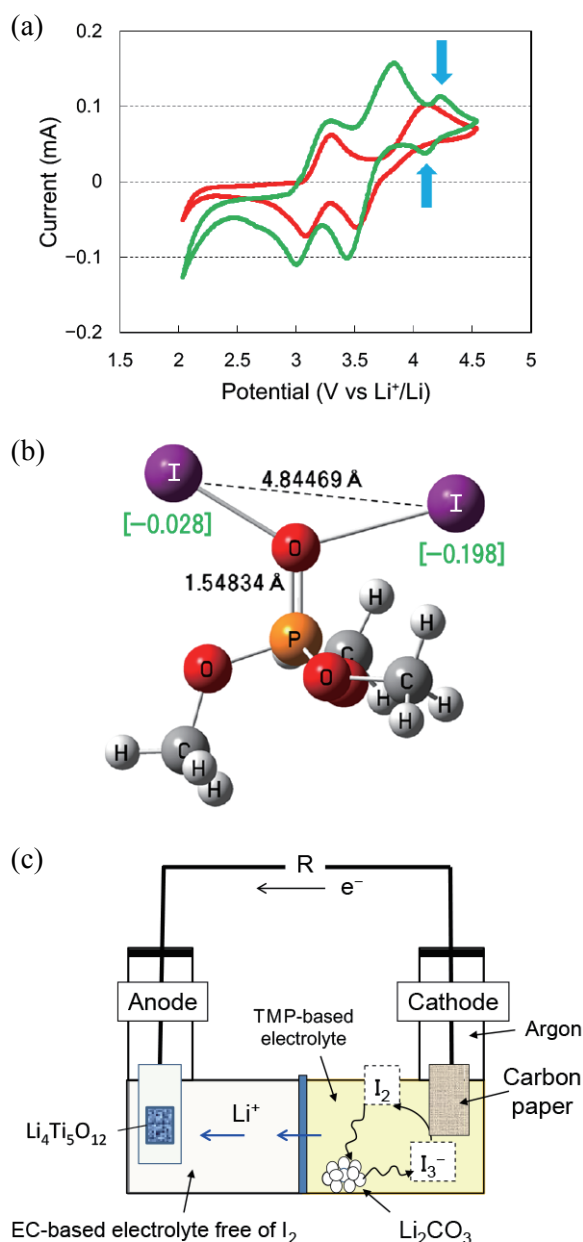
the MgO had been decomposed by the iodine in the DMSO. Since the $I_3$ ions that are produced during the reaction with MgO can transition back to $I_2$ as a result of an electrical charge (i.e., can act as a redox mediator), a catalytic cycle combining this phenomenon with electrical charging could be designed to permit the removal of MgO (Fig. 6(b)). The feasibility of using this catalytic cycle during the charging of a Mg-$O_2$ battery was verified in our lab by adding a small amount of iodine to the LiTFSA-DMSO electrolyte in a Mg-$O_2$ battery. As shown in Fig. 6(c), this modification resulted in the first-ever demonstration of a rechargeable Mg-$O_2$ battery. In other trials of various charging catalysts, we determined that a TEMPO$^+$X$^-$ complex could also serve as a redox mediator and a polymer having TEMPO$^+$X$^-$ units as side chains was added to the carbon cathode. We also succeeded in recharging non-aqueous Ca-$O_2$ systems as well as Mg-$O_2$ batteries.[29,30]

## 2. 5　Observation of Iodine Species with High Redox Potential

The increasing worldwide adoption of electric vehicles is expected to dramatically increase the demand for lithium-ion batteries (LiBs). This demand, in turn, could potentially exhaust existing lithium resources in the near future, and there are also concerns related to environmental destruction due to lithium mining.[31,32] One option to address these issues is lithium reuse. Lithium compounds such as lithium carbonate ($Li_2CO_3$) and lithium fluoride (LiF) are found in spent LiBs[33,34] and Li recovery from these deactivated lithium compounds could allow Li recycling. Section 2.4, above, describes a catalytic system that employs an iodine redox mediator in various solvents. During such work, we happened to observe three redox potentials associated with iodine species in trimethyl phosphate (TMP) solutions (**Fig. 7**(a)).[35] The highest potential of approximately 4.0 V vs. Li$^+$/Li was not observed in $I_2$-propylene carbonate (PC) solutions and we subsequently performed computational studies to understand why the potentials increased in the TMP solution. The Mulliken electric charge distributions for all elements in a 1:1 complex as determined from these calculations are displayed in Fig. 7(b). Since the electric charges of the two iodine atoms in the 1:1 $I_2$-TMP complex were −0.028 and −0.198, there is obviously a significant electric charge distribution

(0.170 = −0.028 − (−0.198)) in this complex. These results suggest that the surprisingly high redox potential of iodine in a TMP solution is caused by a polarization effect resulting from complex formation. Because the anomalously high redox potential associated with this system is larger than the decomposition potential of $Li_2CO_3$ (3.82 V), as calculated from the Nernst equation based on the reaction $Li_2CO_3 \rightarrow 2Li^+ + 2e^- + CO_2 + 0.5O_2$, it is evident that $I_2$ in TMP should be able to oxidize $Li_2CO_3$ (that is, should promote chemical decomposition). We performed experimental trials to verify $Li_2CO_3$ decomposition based on the use of iodine species as a redox couple and a mediator (Fig. 7(c)) and this cell was found to be rechargeable due to the decomposition of $Li_2CO_3$.[36] Thus, although this was not the main focus of our work, this $Li_2CO_3$ decomposition technique was applied to improve the charging properties of Li-$CO_2$ batteries.[37]

## 3. Conclusion

Shortly after joining Toyota CRDL, my supervisor expressed his desire that I would become a good researcher and discover new phenomena. Throughout my career, I kept this encouragement in mind as I engaged in various research and development activities. Looking back, my research theme changed every few years but all the themes were somehow related to the study of materials. I felt it was important to keep a strong sense of inquiry while retaining a humble attitude working in this field, and I am grateful for the opportunity to do so. I believe my workplace fostered my capacity for creativity and provided inspiration, and I hope that my contributions to science will be of some assistance to other researchers throughout the world.



**Fig. 7** (a) CV curves for $I_2$-PC (red) and $I_2$-TMP (green) solutions, (b) electric charge distribution for two iodine atoms in $I_2$-TMP complex, and (c) schematic illustration of $Li_2CO_3$ decomposition system.

## References

(1) Hamlen, R. P., Kent, C. E. and Shafer, S. N., *Nature*, Vol. 206 (1965), pp. 1149-1150.
(2) Tanaka, T., Nishio, I., Sun, S-T. and Ueno-Nishio, S., *Science*, Vol. 218, No. 4571 (1982), pp. 467-469.
(3) Shiga, T. and Kurauchi, T., *Polymer Preprints, Japan*, Vol. 34 (1985), p. 509.
(4) Shiga, T. and Kurauchi, T., *J. Appl. Polym. Sci.*, Vol. 39, No.11-12 (1990), pp. 2305-2320.
(5) Doi, M., Matsumoto, M. and Hirose, Y., *Macromolecules*, Vol. 25, No. 20 (1992), pp. 5504-5511.
(6) Shiga, T., *Advances in Polymer Science*, Vol. 134 (1997), pp. 133-162, Springer.
(7) Klass, D. L. and Martinek, T. W., *J. Appl. Phys.*, Vol. 11 (1967), pp. 319-325.
(8) Uejima, H., *J. Appl. Phys.*, Vol. 14 (1972), pp. 290-292.

(9) Yamamoto, S., Matsuoka, T., Takahashi, H. and Kurauchi, T., *J. Geol. Soc. Jpn.*, Vol. 13 (1992), pp. 2056-2060.

(10) Shiga, T., Ohta, T., Hirose, Y., Okada, A. and Kurauchi, T., *J. Mater. Sci.*, Vol. 28, No. 5 (1993), pp. 1293-1299.

(11) Shiga, T., Okada, A. and Kurauchi, T., *Macromolecules*, Vol. 26, No. 25 (1993), pp. 6958-6963.

(12) Shiga, T. and Okada, A., *J. Appl. Polym. Sci.*, Vol. 62, No. 6 (1996), pp. 903-910.

(13) Shiga, T., Okada, A. and Kurauchi, T., *J. Appl. Polym. Sci.*, Vol. 58, No. 4 (1995), pp. 787-792.

(14) Rughooputh, S. D. D. V., Nowak, M., Hotta, S., Heeger, A. J. and Wudl, F., *Synth. Met.*, Vol. 21, No. 1-3 (1987), pp. 41-50.

(15) Yoshino, K., Nakajima, S., Onoda, M. and Sugimoto, R., *Synth. Met.*, Vol. 28, No. 1-2 (1989), pp. 349-357.

(16) Swanson, L. S., Shinar, J. and Yoshino, K., *Phys. Rev. Lett.*, Vol. 65, No. 9 (1990), pp. 1140-1143.

(17) Shiga, T., Okada, A., Takahashi, H. and Kurauchi, T., *J. Mater. Sci. Lett.*, Vol. 14, No. 24 (1995), pp. 1754-1756.

(18) Shiga, T., Ikawa, T. and Okada, A., *J. Appl. Polym. Sci.*, Vol. 67, No. 2 (1998), pp. 259-266.

(19) Mittal, K. L., *Adhesion Aspects of Polymeric Coatings*, Vol. 2 (2003), 203p. Utrecht.

(20) Shiga, T., Narita, T., Tachi, K., Okada, A., Takahashi, H. and Kurauchi, T., *Polym. Eng. Sci.*, Vol. 37, No. 1 (1997), pp. 24-30.

(21) Shiga, T., Narita, T., Ikawa, T. and Okada, A., *Polym. Eng. Sci.*, Vol. 38, No. 4 (1998), pp. 693-698.

(22) Ikawa, T., Shiga, T. and Okada, A., *J. Appl. Polym. Sci.*, Vol. 83, No. 12 (2002), pp. 2600-2603.

(23) Lu, J., Li, L., Park J-B., Sun, Y-K, Wu, F. and Amine, K., *Chem. Rev.*, Vol. 114, No. 11 (2014), pp. 5611-5640.

(24) Luntz, A. C. and McCloskey, B. D., *Chem. Rev.*, Vol. 114, No. 23 (2014), 11721-11750.

(25) Mulliken, R. S., *J. Am. Chem. Soc.*, Vol. 72, No. 1 (1950), pp. 600-608.

(26) Lewis, C. and Skoog, D. A., *J. Am. Chem. Soc.*, Vol. 84, No. 7 (1962), pp. 1101-1106.

(27) Drago, R. S., Wayland, B. and Carlson, R. L., *J. Am. Chem. Soc.*, Vol. 85, No. 20 (1963), pp. 3125-3128.

(28) Shiga, T., Hase, Y., Kato, Y., Inoue, M. and Takechi, K., *Chem. Commun.*, Vol. 49, No. 80 (2013), pp. 9152-9154.

(29) Shiga, T., Hase, Y., Yagi, Y., Takahashi, N. and Takechi, K., *J. Phys. Chem. Lett.*, Vol. 5, No.10 (2014), pp. 1648-1652.

(30) Shiga, T., Kato, Y. and Hase, Y., *J. Mater. Chem. A*, Vol. 5, No. 25 (2017), 13212-13219.

(31) Kim, J-S., Lee, Y-H., Choi, S., Shin, J., Dinh, H-C. and Choi, J. W., *Environ. Sci. Technol.*, Vol. 49, No.16 (2015), pp. 9415-9422.

(32) Ryu, T., Haldorai, Y., Rengaraj, A., Shin, J., Hong, H-J., Lee, G-W., Han, Y-K., Huh, Y. S. and Chung, K-S., *Ind. Eng. Chem. Res.*, Vol. 55, No. 26 (2016), pp. 7218-7225.

(33) Xu, K., *Chem. Rev.*, Vol. 114, No. 23 (2014), 11503-11618.

(34) Aravindan, V., Gnanaraj, J., Lee, Y-S. and Madhavi, S., *Chem. Rev.*, Vol. 114, No. 23 (2014), 11619-11635.

(35) Shiga, T., Kato, Y., Inoue, M. and Takechi, K., *J. Power Sources*, Vol. 217, No. 1 (2012), pp. 538-542.

(36) Shiga, T., Kondo, H., Kato, Y. and Hase, Y., *J. Phys. Chem. C*, Vol. 123, No. 7 (2019), pp. 3944-3950.

(37) Shiga, T., Kato, Y., Inoue, M. and Hase, Y., *ACS Sustainable Chem. Eng.*, Vol. 7, No. 16 (2019), 14280-14287.

Figs. 6(a) and (c)
Adopted from Chem. Commun., Vol. 99 (2013), 9152, Shiga, T., Hase, Y., Kato, Y., Inoue, M. and Takechi, K., A Rechargeable Non-aqueous Mg–O$_2$ Battery, © 2013 RSC, with permission from The Royal Society of Chemistry.

Fig. 7(b)
Adopted from J. Phys. Chem. C, Vol. 123 (2019), pp. 3944-3950, Shiga, T., Kondo, H., Kato, Y. and Hase, Y., Iodine Mediator with Anomalously High Redox Potential and Its Application to a Catalytic Cycle for Lithium Carbonate Decomposition toward Future Lithium Reproduction, © 2019 ACS, with permission from American Chemical Society.

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