

In-Situ Infrared Spectroscopic Studies of Electrochemical Energy Conversion and Storage

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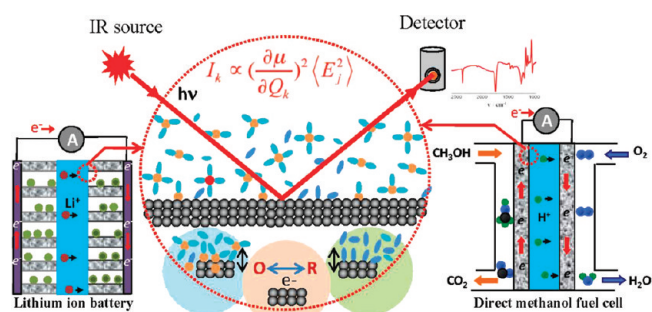
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CONSPECTUS

With their ability to convert chemical energy of fuels directly into electrical power or reversibly store electrical energy, systems such as fuel cells and lithium ion batteries are of great importance in managing energy use. In these electrochemical energy conversion and storage (EECS) systems, controlled electrochemical redox reactions generate or store the electrical energy, ideally under conditions that avoid or kinetically suppress side reactions. A comprehensive understanding of electrode reactions is critical for the exploration and optimization of

electrode materials and is therefore the key issue for developing advanced EECS systems. Based on its fingerprint and surface selection rules, electrochemical in-situ FTIR spectroscopy (in-situ FTIRS) can provide real-time information about the chemical nature of adsorbates and solution species as well as intermediate/product species involved in the electrochemical reactions. These unique features make this technique well-suited for insitu studies of EECS.

In this Account, we review the characterization of electrode materials and the investigation of interfacial reaction processes involved in EECS systems by using state-of-the-art in-situ FTIR reflection technologies, primarily with an external configuration. We introduce the application of in-situ FTIRS to EECS systems and describe relevant technologies including in-situ microscope FTIRS, in-situ time-resolved FTIRS, and the combinatorial FTIRS approach. We focus first on the in-situ steady-state and time-resolved FTIRS studies on the electrooxidation of small organic molecules. Next, we review the characterization of electrocatalysts through the IR properties of nanomaterials, such as abnormal IR effects (AIRES) and surface enhanced infrared absorption (SEIRA). Finally, we introduce the application of in-situ FTIRS to demonstrate the decomposition of electrolyte and (de)lithiation processes involved in lithium ion batteries. The body of work summarized here has substantially advanced the knowledge of electrode processes and represents the forefront in studies of EECS at the molecular level.



1. Introduction

Electrochemical energy conversion and storage (EECS), especially direct organic fuel cells (DOFCs) and lithium ion batteries (LIBs), are technologies of growing importance. DOFCs are devices that convert the chemical energy of small organic molecules (SOMs) directly into electricity, producing only water and CO₂ as waste. LIBs directly transform chemical to electrical energy and vice versa. Normally, LIBs and DOFCs contain an anode and a cathode which are separated by either an absorbent material soaked with

electrolyte solution or an ion exchange membrane. The electrical energy is generated/stored via controlled redox reactions at each electrode–electrolyte interface, where electron and ion transport are separated. At any time, a number of reactions may simultaneously occur at the electrode–electrolyte interface. In an ideal EECS system, the target reaction would occur with all others kinetically suppressed. In-situ monitoring of liquid–solid interface processes is essential for the successful development of EECS. Beyond the traditional electrochemical methods that

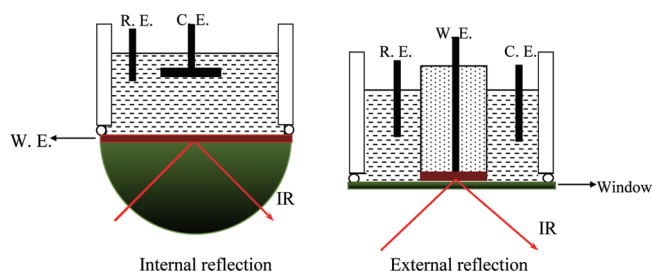


FIGURE 1. Schematic diagrams of in-situ FTIRS cell with internal and external reflection configurations.

only provide potentiometric and amperometric data, in-situ FTIRS allows characterization of molecules, adsorbates, and reaction intermediates, thereby enhancing our knowledge of interfacial processes. Pioneered by Bewick et al. in the early 1980s,^{1,2} a number of studies have extended the in-situ FTIRS methods from smooth to rough surfaces, from static to dynamic conditions, and from aqueous to nonaqueous systems. Successful implementation of FTIRS to the EECS solid–liquid interface requires overcoming several fundamental issues associated with signal-to-noise ratio: (1) reflected IR energy is strongly absorbed by solution electrolyte species; (2) IR energy is partially lost during its reflection at the electrode surface; (3) the IR signal from (sub)monolayer adsorbed species on the electrode surfaces is very weak. Besides the use of highly reflective electrodes, the employment of weak signal determination methods such as potential or polarization modulation could improve the signal-to-noise ratio of spectra.

Two approaches toward cell design have been applied to minimize the strong absorption by electrolyte species. These are the internal and external reflection configurations, schematic diagrams of which are presented in Figure 1. In the external reflection configuration, the electrode sample is placed in close contact with the light guiding prism; the thin layer (1–10 μm) ensures a short path length through the liquid and maximum IR illumination of the sample. This approach has the advantages of access to a wider range of electrode materials and simultaneous determination of both adsorbed and solution species involved in the EECS reactions. Although the mass transport may be seriously restricted between the thin layer and the reservoir, the use of a microelectrode can partially overcome this limitation.³ Internal reflection with the attenuated total reflection (ATR) mode is also employed for sampling in infrared spectroscopy, in which a thin metal film deposited on an IR transparent prism with high refractive index is used as the working electrode.^{4,5} Since the IR beam is focused at the interface from the back of the electrode (through the prism) and the

reflected radiation is then detected, a thick solution layer can be used, which gives a rapid potential response and facilitates free mass transport. ATR mode is also applied to characterize the Pt/Nafion membrane interface during the oxygen electroreduction.⁶ In this Account, we concentrate on the characterization of electrode materials and investigation of interfacial reaction processes involved in EECS through the use of in-situ FTIRS.

2. In-Situ FTIRS Studies of Electrocatalysis in Electrochemical Energy Conversion

Pt and its alloys are currently used as indispensable catalysts for DOFCs. The key objectives in electrocatalysis of DOFCs are to reduce Pt loading and improve the catalyst's efficiency. It is, thus, important to investigate in situ the interfacial processes and the surface structure-catalytic functionality. Studies performed using FTIRS are key to this end, starting from mirror-polished metallic electrodes, and onto nanostructured electrodes, commercial catalysts, i.e., the multimetallic particles dispersed on a conductive carbon material, and finally real fuel cells (operando observation⁷). The dual-path mechanism and active/poisoning intermediates in the electrooxidation of SOMs have been well characterized by in-situ FTIRS methods.^{8,9} Generally, in-situ FTIRS studies are concerned with the dissociative adsorption and oxidation of organic molecules, the formation, adsorption, and oxidation of intermediates, the nature of adsorbed species and their interaction with catalysts, the determination of reaction selectivity, and also effects of catalyst composition, size, and morphology.

2.1. Steady-State Characterization. Typically IR adsorption, which is related to the status of the electrode surface or the electrochemical reactions at a given electrode potential in SOM electrooxidation, is detected by steady-state infrared spectra.^{10–12} Steady-state infrared technologies include subtractively normalized interfacial FTIRS (SNIFTIRS),¹³ single potential alteration FTIRS (SPAFTIRS),¹⁴ and multistep FTIRS (MS-FTIRS).¹⁵ Recent approaches to probe the reaction intermediates and pathways on new kinds of electrocatalyst and fuel molecules by in-situ FTIRS were devised to aid mechanistic insight in the electrooxidation of SOMs.

SOM Containing C–C Bonds. The essence of SOM electrooxidation is the breaking of C–H and C–C bonds as well as the formation of C–O and H–O bonds. Ethanol is an example of a 2 C atom reactant which undergoes structure and composition sensitive parallel reactions during its electrooxidation.¹⁶ Breaking of the C–C bond, which is

necessary to complete oxidation of the molecule to CO_2 , is the principal challenge for direct ethanol fuel cells. By contrast, soluble acetaldehyde and acetic acid are the main products in the partial oxidation pathway reactions. Recent studies have shown that Pt nanoparticles (NPs) enclosed by high-index-facets exhibit enhanced catalytic activity toward electrooxidation of organic fuels.¹⁷ The electrocatalytic activity and pathway for ethanol electrooxidation on high-index-faceted Pt NPs supported on carbon black (HIF-Pt/C) and commercial Pt/C catalysts were compared by in-situ FTIRS (Figure 2).¹⁰ The upward band at 1044 cm^{-1} is the signature peak for the C–O stretching ($\nu_{\text{C-O}}$) of ethanol, representing the oxidative consumption of ethanol. The CO_2 downward band at 2343 cm^{-1} reflects cleavage of the C–C bond of ethanol. The stretching of the C=O bond ($\nu_{\text{C=O}}$) near 1720 cm^{-1} is indicative of acetic acid and acetaldehyde. The band at 1280 cm^{-1} is the characteristic absorption of $\nu_{\text{C-O}}$ in

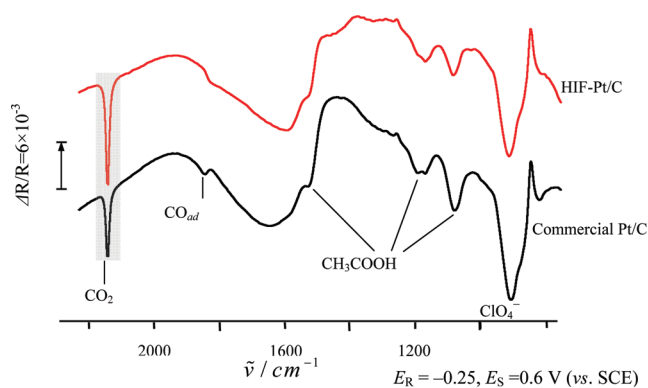
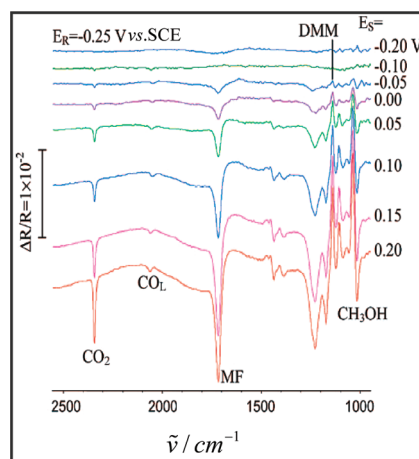


FIGURE 2. In-situ FTIR spectra of ethanol oxidation on HIF-Pt/C and commercial Pt/C at 0.60 V in 0.1 M ethanol + 0.1 M HClO_4 .

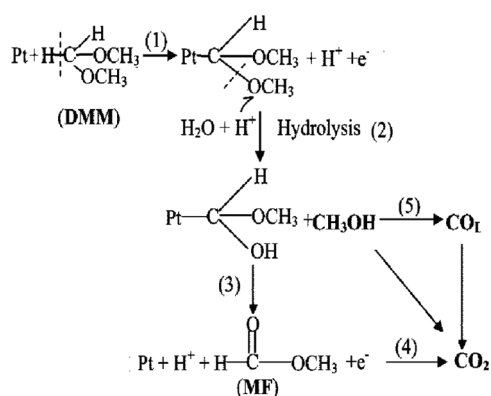
acetic acid. More CO_2 and less acetic acid are formed on HIF-Pt/C catalysts during ethanol oxidation in comparison with commercial Pt/C catalysts. The ratio of band intensities of CO_2 to acetic acid on HIF-Pt/C is twice that of the commercial Pt/C. The in-situ FTIRS results therefore reveal that the HIF-Pt/C catalysts have enhanced activity for breaking the C–C bond in ethanol.

In-situ FTIRS can also be used for the manipulation of electrocatalytic pathways of SOM using surface chemistry.¹² For the oxidation of 1,3-butanediol on Sb and S adatom modified Pt electrodes (Pt/Sb_{ad} and Pt/S_{ad}), the in-situ FTIRS spectra demonstrated that the dissociative reaction of 1,3-butanediol into adsorbed CO has been inhibited on both electrodes. For the oxidation of 1,3-butanediol via reactive intermediates (evidenced by new IR bands of $\nu_{\text{C-H}}$, $\nu_{\text{C=O}}$, $\nu_{\text{C-O}}$), the oxidation could be completed producing CO_2 on the Pt/Sb_{ad}, while on the Pt/S_{ad} the reaction is shown to yield mainly carbonyl species.

SOM without C–C Bonds. The electrooxidation of dimethoxymethane (DMM) and methanol do not require the breaking of a C–C bond. DMM is regarded as a promising new fuel for DOFCs as it has a higher energy density, lower toxicity, and lower crossover than methanol and is commonly available from coal/natural gas. Figure 3a shows in-situ FTIR spectra of DMM electrooxidation on the Pt electrode at different potentials.¹¹ Three upward bands at 1138, 1106, and 1035 cm^{-1} are assigned to DMM ($\nu_{\text{C-O-C-O}}$), indicating its consumption. Five downward bands at 1717, 1435, 1385, 1227, and 1172 cm^{-1} are attributed to methyl formate (MF) formation. CO_2 (2343 cm^{-1}) is the complete oxidation product of DMM. The downward band at



(a)



(b)

FIGURE 3. In-situ FTIR spectra of DMM electrooxidation on a Pt electrode in 0.1 M DMM + 0.1 M H_2SO_4 solution and its proposed electrooxidation reaction mechanism.

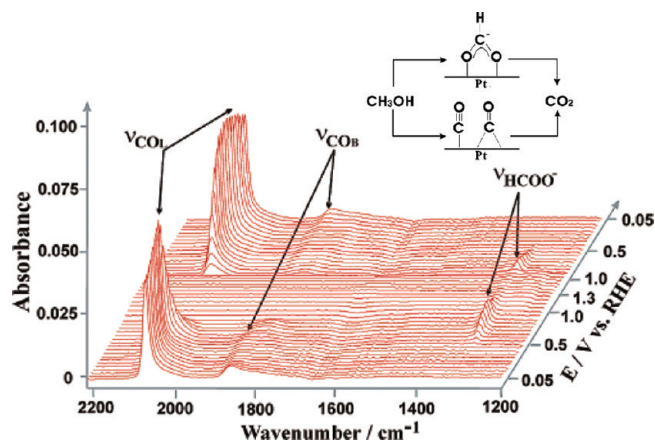


FIGURE 4. IR spectra of the Pt/solution interface during methanol electrooxidation on Pt, and reaction pathways of methanol oxidation at Pt electrode.

1016 cm^{-1} is assigned to methanol ($\nu_{\text{C-O}}$) that may be generated by the hydrolysis of methoxyl groups in DMM or MF species. A band at about 2070 cm^{-1} , whose center is shifted with the potential, can be assigned to linearly bonded CO (CO_L). The above FTIR studies demonstrate that MF, CO_2 , and methanol are the main solution phase products and CO_L is an adsorbed intermediate for DMM oxidation on Pt electrode in H_2SO_4 solution. According to the variation of related peak intensities with electrode potential, in-situ FTIR results further indicate that DMM is preferentially oxidized incompletely to methyl formate, which is difficult to oxidize further. Moreover, one methoxyl group in DMM undergoes hydrolysis to form methanol that can be oxidized to CO_2 , or can generate linearly bonded CO through dissociative adsorption. Based on in-situ FTIRS observations, a reaction mechanism for DMM electrooxidation in acidic solution is proposed in Figure 3b.

Studies of methanol electrooxidation by Lamy et al. have revealed CO_L , small amounts of formaldehyde and formic acid, dependent on alloy composition.¹⁸ Much progress in the elucidation of the oxidation mechanism of methanol on Pt surfaces was made by Osawa and co-workers, who successfully detected adsorbed formate as the reactive intermediate.¹⁹ They used in-situ surface-enhanced IR absorption spectroscopy, a tool very sensitive to adsorbed species. As shown in Figure 4, besides CO_L and bridge-bonded CO (CO_B), a weak band appears around 1320 cm^{-1} . The peak position of this band was found to shift with electrode potential, indicating that this band comes from adsorbed species. Furthermore, this band shifted to 1300 cm^{-1} when CD_3OH or $^{13}\text{CH}_3\text{OH}$ was used instead of CH_3OH , indicating that the adsorbed species contained both H and C

atoms. Based on these results, the authors attributed this band to adsorbed formate and proposed reaction pathways for methanol oxidation at the Pt electrode.

2.2. Kinetics and Dynamics Processes. In-situ time-resolved FTIRS can provide both structural and transient information, which offers the potential to obtain dynamic molecular information.^{20,21} Significant efforts have been dedicated to the development of electrochemical in-situ time-resolved IR techniques whereby transient information on short-lived intermediates and dynamic processes can be obtained for a wide variety of electrochemical reactions. The spectral time-resolution (t_R) of in-situ FTIRS is not only limited by the performance of the FTIR spectrometer and the methodology of spectral data collection, but more significantly by the double-layer charging of electrode–electrolyte interface. In practice, electrochemical response depends remarkably on the configuration of the IR electrolytic cell, i.e., ATR or thin layer cell. Owing to rapid potential response and free mass transfer, IR cells of ATR configuration currently predominate in temporal measurements.²² As stated above, a disadvantage of the ATR configuration is the limited scope of suitable electrodes. Although the large time constant of the conventional thin-layer IR cell has greatly hampered its application in transient investigations, the employment of IR microscopes with microelectrodes exhibiting excellent transient performance makes it possible for thin-layer IR cells to be applied in transient investigations. Two types of in-situ time-resolved IR spectroscopy based on microscopy FTIRS and microelectrodes and utilizing thin-layer IR cells have been developed, namely, in-situ step-scan time-resolved FTIRS (SSTR-FTIRS) and rapid-scan time-resolved FTIRS (RSTR-FTIRS).

RSTR-FTIRS. RSTR-FTIRS is a convenient time-resolved technique, which employs the highest velocity of the moving mirror to shorten the scan duration that determines the spectral time resolution. The mirror of the interferometer moves in a linear scan mode with constant velocity. For the Nexus 870 FTIR spectrometer, the highest velocity is about 8.22 cm s^{-1} that provides a t_R of 13 ms at 16 cm^{-1} , or 21 ms at 8 cm^{-1} . Therefore, a dynamic process with a half-life of about 100 ms can be studied using RSTR-FTIRS. The main advantage of in-situ RSTR-FTIRS is that it can readily be used to monitor irreversible electrochemical reactions.

Zhou et al. reported a RSTR-FTIRS study of the dynamic processes of methanol oxidation, using a FTIR spectrometer with rapid-scan facility and an IR microscope in combination with a nanostructured Pt microelectrode (*nm*-PtME).²³ This technology successfully overcomes the disadvantages in

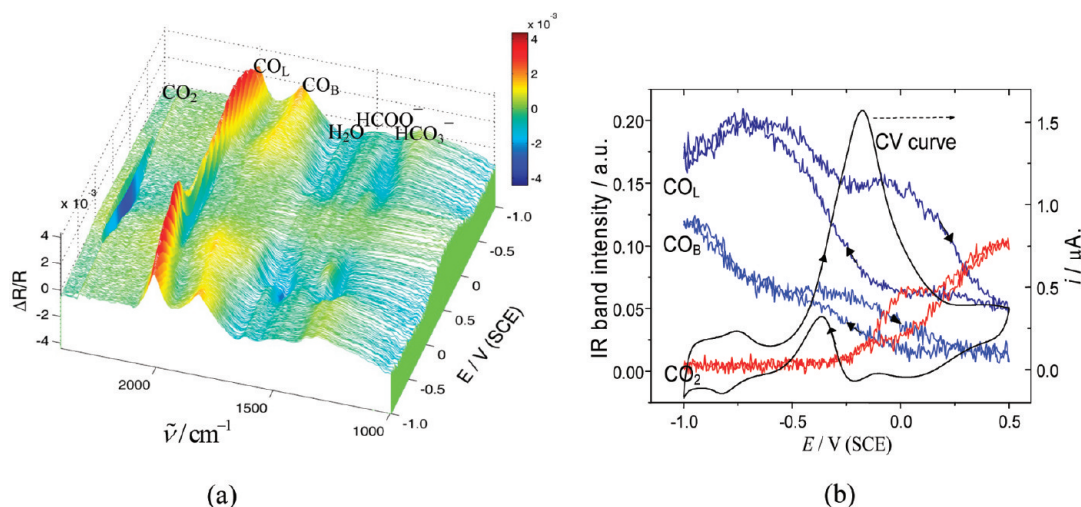


FIGURE 5. (a) Three-dimensional plot of in-situ RSTR-FTIR spectra of methanol oxidation on *nm*-PtME in 0.1 M CH₃OH + 0.1 M NaOH, $E_R = -1.0$ V, with potential interval of 2.6 mV and scan rate 200 mV s⁻¹. (b) IR band intensity of CO_L, CO_B, and CO₂ with E_S .

mass transport, transient response, and uniformity of current flow that arise from a conventional external reflection infrared cell. Figure 5 illustrates in-situ RSTR-FTIR spectra collected simultaneously with cyclic voltammograms (CVs) for methanol oxidation on *nm*-PtME in alkaline solution. The results illustrate that CVs and infrared spectra within a potential interval of 2.6 mV can be simultaneously recorded at a potential scan rate up to 200 mV s⁻¹. The dynamic processes of the adsorbed CO and formate ions involved in methanol oxidation in alkaline solutions were studied intensively. It was revealed that the CO_B species and formate ions are generated preferentially at the onset potential (0.54 V vs SCE) of methanol oxidation, while the CO_L species originate at more positive potentials that are close to the anodic current peak potential (0.17 V vs SCE) of methanol oxidation.

SSTR-FTIRS. The key feature of SSTR-FTIRS is that the spectral data are collected as a function of time when the moving mirror of the interferometer in the FTIR apparatus is completely stopped. With each step of the moving mirror, the reaction processes under study is simultaneously initiated and time-resolved spectral data are recorded. Finally, the spectral data are assembled into an interferogram, and a series of time-resolved single-beam spectra are obtained through Fourier transformation of all interferograms in the time sequence of the progressing reaction. The t_R of SSTR-FTIRS is independent of mechanical response of the interferometer and mainly limited by a slow response to potential change and poor mass transport in the thin-layer region between the electrode and IR window. In an attempt to improve system time response, an *nm*-PtME (200 μm in diameter)

was sealed into a glass capillary with a thickness of 30 μm and fabricated for use as the working electrode. By using adsorbed CO as a probe molecule, a best measured t_R value of 10 μs has been achieved, as determined from the shift of the CO band with electrode potential.²⁴

Electrooxidation of SOM is irreversible; however, in principle, reaction processes studied by SSTR-FTIRS must be repeated reversibly several hundred to several thousand times. Through the combination of a specially designed thin-layer IR flow cell and a nanostructured microelectrode, the solution in the thin layer between the IR window and microelectrode as well as the adsorbates on electrode surface can be rapidly renewed, allowing irreversible reactions to be repeated quickly (Figure 6a). To demonstrate the application of SSTR-FTIRS in an irreversible system, CO_{ad} was chosen for electrooxidation.³ The dynamic process of CO oxidation on an *nm*-PtME in acid solution was studied as a test reaction to illustrate the performance of the newly developed in-situ SSTR-FTIRS technology. Figure 6b shows in-situ SSTR-MFTIR spectra with a time resolution of 250 μs for adsorbed CO oxidation on *nm*-PtME at 1.0 V (vs SCE). At such a high overpotential, the oxidation of CO occurs too quickly to be monitored by conventional time-resolved FTIRS. The CO_L band at 2103 cm⁻¹ quickly vanished within 20 ms. It can be seen that the IR band center of CO slightly decreases with time within the initial 4 ms and then maintains a constant value as the oxidation reaction proceeds. The coverage-independent band center of CO indicates that the CO on the Pt surface is distributed in an island structure, which rules out the oxidation reaction via the generally accepted Langmuir–Hinshelwood mechanism at low

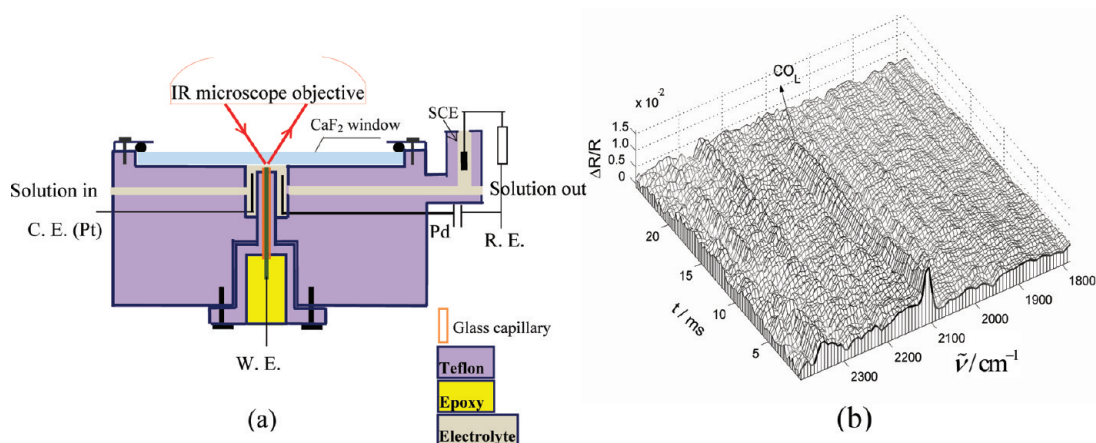


FIGURE 6. (a) Schematic diagrams of SSTR-MFTIR cell for the irreversible process. (b) Three-dimensional plot of in-situ SSTR-MFTIR spectra of CO_{ad} oxidation on nm -PtME in 0.1 M H_2SO_4 , $t_{\text{R}} = 250 \mu\text{s}$, E_{S} was stepped from 0.40 to 1.0 V, $E_{\text{R}} = 1.0$ V.

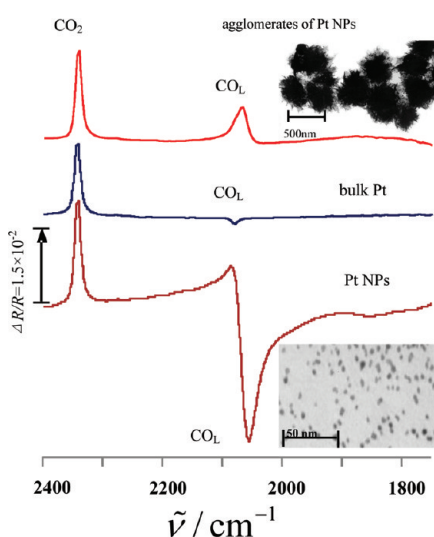


FIGURE 7. CO bands on bulk Pt, Pt NPs, and agglomerates of Pt NPs.

overpotential. In contrast, CO oxidation on the Pt surface proceeds mainly through a nucleation and growth mechanism at high overpotentials due to insufficient time for the relatively slow surface diffusion of the adsorbed CO.

2.3. Characterization of Nanostructured Electrocatalysts. In-situ FTIRS can also be used to characterize exceptional properties of nanomaterials, if a suitable probe molecule is employed. The adsorption of CO on transition metals leads to the formation of a 5σ bond and a $d-\pi^*$ back-donation. This configuration is highly sensitive to local physicochemical stimuli and provides a model system for studies in surface science and related disciplines. CO_{ad} as a probe molecule on the surface of transition metals has proven invaluable in IR spectroscopy, since the $\text{C}\equiv\text{O}$ stretching mode absorbs intensely. Sun et al. were the first to discover that nm -Pt thin films exhibited abnormal IR effects

(AIREs).²⁵ That is, CO adsorbed on nm -Pt and nm -Pd thin films gives rise to three abnormal IR characteristics in comparison with normal IR spectra on bulk Pt electrodes: (1) complete inversion of direction of the CO_{ad} bands, (2) significant enhancement of the IR absorption of CO_{ad} , and (3) increase in full width at half-maximum (fwhm) of IR bands. In follow-up studies, the AIREs were also found on nm -platinum group and iron-triad metals, such as Pt, Pd, Ru, Rh, Os, Ir, Ni, and Co.^{26–31} Besides the AIREs, the surface enhanced infrared absorption (SEIRA), first documented by Hartstein et al. in 1980,³² was extensively reported and well-illustrated by Osawa and co-workers³³ and Cai et al.³⁴ In comparison with IRRAS, SEIRAS and AIREs have a higher surface selectivity and sensitivity; thus, the interface/surface reactions can be selectively monitored with less interference from the bulk solution.

IR properties of adsorbed CO depend strongly on the interaction between NPs, as well as NPs' size/structure and the thickness of the nm -film. Figure 7 compares the adsorbed CO on bulk Pt, dispersed NPs, and agglomerates of Pt NPs.²⁶ The upward CO_2 band (2345 cm^{-1}), the downward CO_L band (ca. 2059 cm^{-1}), and a small but broad downward band CO_B (near 1855 cm^{-1}) are observed. The intensities of CO_{ad} on Pt NPs and its agglomerates are both enhanced. On agglomerates of Pt NPs, an inverted upward CO_L band is observed in comparison with the bands exhibited by the bulk Pt and dispersed Pt NPs. The above results demonstrate that the dispersed Pt NPs and their agglomerates exhibit significantly different IR optical properties. AIREs observed exclusively on agglomerated NPs may be ascribed primarily to the strong interaction between Pt NPs and the collective

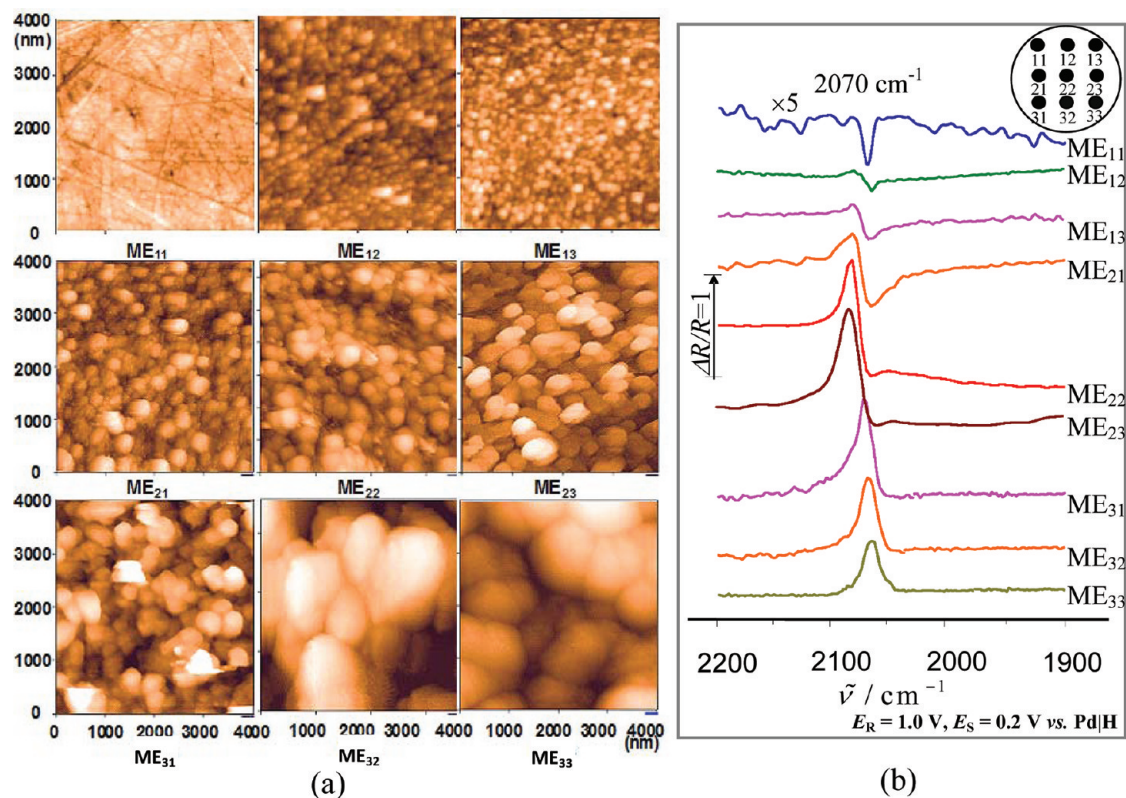


FIGURE 8. Combinatorial studies of the structures (a) and IR properties (b) on *nm*-Pt films of an individual array.

interaction between CO adsorbates and the Pt NPs forming the agglomerates.

To systemically investigate the IR properties of nanostructures, an approach of combinatorial spectroelectrochemical analysis has been developed by combining in-situ microscope FTIR spectroscopy with an individually addressable array of microelectrodes.^{35,36} This method was applied successfully for an investigation of the anomalous IR properties of nanostructured film materials of Pt and Ru. Different nanostructures were prepared on an individually addressable array (3×3) of PtMEs. Figure 8 compares the structure and IR properties of CO on *nm*-Pt.³⁶ The main consequence of these treatments was the creation of nanoislands on the PtMEs; the longer the treatment time, the larger the size of these Pt nanoislands. The IR features of the CO_L band (ca. 2070 cm^{-1}) progressively varied with the surface nanostructures of PtME on the array, including (1) the direction and shape of the CO_L band are turned from the downward monopolar to bipolar and finally to upward monopolar; (2) the fwhm of CO_L band is broadened; (3) the change of Stark tuning rate is progressively decreased; and (4) the intensity of the CO_L band is initially enhanced and then reduced.

These results demonstrate that anomalous IR behavior is strongly correlated with nanomaterial size/structure. It is reasonable to assume that some intrinsic correlations exist behind the highlighted IR effects. Recently, the electron–hole mechanism and the effective medium theory were introduced to formulate a simulation of the AIREs *nm*-thin films.^{37,38}

3. In-Situ FTIRS Studies of Interfacial Processes Involved in Electrochemical Energy Storage

The performance and safety of LIBs are dependent on the structures and process of their nonaqueous interfacial reactions, including insertion/extraction of lithium ions, solvation/desolvation of lithium ions, decomposition of the electrolyte, and formation/variation of the surface layer. On the electrode materials, the electrochemical decomposition of electrolyte solution occurs during the cycling process, resulting in the formation of the so-called solid electrolyte interphase (SEI) layer. The chemical composition of these materials as well as their variation with electrode potential, cycling number, and temperature have been clearly characterized by ex-situ FTIRS. In-situ FTIRS can provide direct real-time information about interfacial reactions on different

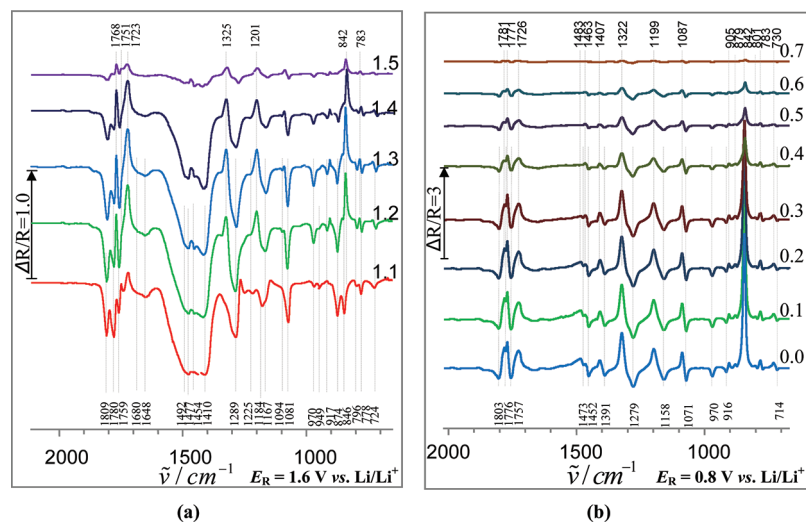


FIGURE 9. In-situ FTIR spectra of electroplated Sn anode during (a) reduction of electrolyte and (b) lithiation process.

kinds of electrode materials of LIBs, and has been focused on investigations of the reaction/oxidation of various electrolytes. Surface layer formation and stripping processes on LiCoO_2 , LiMn_2O_4 , and $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ thin film electrodes were analyzed using in-situ FTIR by Kanamura's group.³⁹ The interfacial process on lithium and MCMB was studied by Morigaki.⁴⁰ Some studies on noble metal and Cu electrodes in nonaqueous systems were also reported by Aurbach et al.⁴¹ However, the air- and waterproof experimental conditions, low IR reflectance of the electrode material, as well as the variation of electrode's surface remain a challenge for these in-situ studies.

Owing to their high reflectivity for incident IR radiation, Sn and Sn-based anodes in 1 M $\text{LiPF}_6/\text{EC}+\text{DMC}$ were analyzed by in-situ FTIR spectroscopy.^{42,43} The processes of electrolyte decomposition and lithiation/delithiation were clearly revealed from in-situ FTIR spectra with a high signal-to-noise ratio. It should be mentioned that the well-known solvation/desolvation processes of lithium ions with the solvent are one of the main reasons for the change of IR adsorption. In the electrolyte, the solvation of Li^+ with electrolyte solvent molecules results in $\text{Li}(\text{sol})_n^+$ species (*sol*: EC, DMC), and the bond of $\text{C}=\text{O}$ is therefore weakened by the coordination of $\text{Li}^+\cdots\text{O}=\text{C}$ in the $\text{Li}(\text{sol})_n^+$ species, leading to a red-shift of $\nu_{\text{C}=\text{O}}$ of $\text{Li}(\text{sol})_n^+$.

Decomposition of Electrolyte. In-situ FTIR spectra of a Sn film electrode during the reduction of electrolyte are shown in Figure 9a. This process is accompanied by the reduction of $\text{Li}(\text{sol})_n^+$ to solid products and the diffusion of free solvents from the bulk into the thin layer. As a consequence, the concentrations of both free solvent and reductive products

increase, while that of $\text{Li}(\text{sol})_n^+$ decreases. Therefore, the downward bands $\nu_{\text{C}=\text{O}}$ (1809, 1780, and 1759 cm^{-1}) and $\nu_{\text{C}-\text{O}}$ (1289, 1167, and 1081 cm^{-1}) should be assigned to free solvents. The broad downward bands located between 1481 and 1416 cm^{-1} may be attributed to $\delta_{\text{C}-\text{H}}$ of free solvents and the reductive products. New downward bands observed at 1648, 1225, 1184, 1094, 949, and 846 cm^{-1} could be assigned to the IR absorption of the reduction products, such as Li_2CO_3 and ROCO_2Li . However, the IR absorption of the reduction products may partially overlap with those of solvent molecules.

Lithiation/Delithiation Processes. When the electrode potential is negatively polarized to 0.8 V (vs Li/Li^+), as stated above, the surface of Sn anode is covered by a SEI layer. If the spectrum collected at 0.8 V is set as the reference spectrum, the IR adsorption by the SEI layer can be excluded. Figure 9b compares in-situ FTIR spectra of Sn in 1 M $\text{LiPF}_6/\text{EC}+\text{DMC}$. When potential is decreased from 0.8 to 0.0 V (vs Li/Li^+), Li desolvates from $\text{Li}(\text{sol})_n^+$ and then alloys with Sn, which results in an increase of free solvent and decrease of $\text{Li}(\text{sol})_n^+$ species. The bands at 1803 and 1766 cm^{-1} are assigned to the $\nu_{\text{C}=\text{O}}$ of free EC, and the band close to 1757 cm^{-1} is attributed to the $\nu_{\text{C}=\text{O}}$ of free DMC. The upward $\nu_{\text{C}=\text{O}}$ bands at 1768 and 1723 cm^{-1} and $\nu_{\text{C}-\text{O}}$ bands at 1325 and 1201 cm^{-1} signify the consumption of $\text{Li}(\text{sol})_n^+$ in the reductive process. The upward peaks at 1781, 1771, and 1726 cm^{-1} can be assigned to $\nu_{\text{C}=\text{O}}$ of $\text{Li}(\text{sol})_n^+$. The $\nu_{\text{C}-\text{O}}$ bands of free DMC and EC at 1279, 1158, and 1071 cm^{-1} are observed in the downward direction, whereas those bands of the $\text{Li}(\text{sol})_n^+$ species are observed in the upward direction at higher wavenumbers of 1322, 1199, and 1087 cm^{-1} . These

blue-shifts indicate that the C–O bond is strengthened by the $\text{Li}^+ \cdots \text{O}=\text{C}$ coordination in $\text{Li}(\text{sol})_n^+$. A strong upward band at 842 cm^{-1} is assigned to the IR absorption of PF_6^- anions. Clearly, the lithiation process was characterized by FTIRS from the desolvation effect which varies the free solvent and $\text{Li}(\text{sol})_n^+$ concentrations. In contrast for the Cu electrode, no significant IR bands are observed, as it cannot alloy with Li during the course of cathodic polarization.⁴³

4. Conclusions

This Account has detailed the development of in-situ FTIRS using mainly external reflection mode and its applications in the investigation of EECS. In the case of the methodology, in-situ microscope FTIR spectroscopy, in-situ time-resolved FTIR spectroscopy, and the surface combinatorial analysis by FTIR spectroscopy have been introduced. The dynamic and static studies of oxidation process of organic fuels, and characterization of electrocatalysts through the anomalous IR properties of nanomaterials were summarized. We have also extended the in-situ FTIRS to study nonaqueous interfacial processes involved in lithium ion batteries.

Further developments of FTIR reflection spectroscopy and applications in the exciting area of EECS may be expected. These include (1) increasing sensitivity for low reflectivity electrodes and low coverage adsorbates; (2) improving spectral time-resolution to probe short-lived intermediates and ultrafast dynamic processes; (3) developing operando methods for inspection of EECS under real-operation conditions; (4) combining in-situ FTIRS with other modern techniques such as SFG, SHG, Raman, and NMR to achieve a comprehensive and thorough understanding of surface structure functionality of nanomaterial electrodes and interfacial processes involved in EECS; and (5) lastly, extending in-situ FTIRS to reactions involved in a wide range of EECS such as supercapacitors, dye-sensitized solar cells, and biofuel cells.

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FOOTNOTES

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