

Advanced Energy Research Section

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1. Summary

The author spent one month at Kyoto University, Uji Campus in Prof. Nohira's group. Here is a summary of the study on the microparticle electrodes and single particle microbatteries using electrochemical and in-situ micro-Raman spectroscopic studies [1].

2. Introduction

The author discuss the study of the electrochemical, structural, and electronic properties of microparticles of energy storage materials for battery applications. This report summarizes efforts toward the development and implementation of methods for the in situ electrical, optical, and spectroscopic characterization of microparticles of materials including nickel hydroxide, zinc, carbon, and lithiated manganese and cobalt oxides. In the case of nickel hydroxide, the darker appearance of NiOOH compared to the translucent character of Ni(OH)₂ allowed for the spatial and temporal evolution of charge flow within spherical microparticles of Ni(OH)₂ to be monitored in real-time. In situ Raman scattering measurements involving single microparticles of zinc revealed that passive films formed in strongly alkaline solutions displayed a largely enhanced feature at approximately 565 cm⁻¹ ascribed to a longitudinal optical phonon mode of ZnO. This effect is associated with the presence of interstitial zinc and oxygen deficiencies in the lattice. Significant amounts of crystalline ZnO could only be detected for passive films formed at the same two potentials after the electrodes had been roughened by a single passivation-reduction step. Quantitative correlations were found in the case of LiMn₂O₄ and KS-44 graphite between the Raman spectral properties and the state of charge. In the case of KS-44, a chemometrics analysis of the spectroscopic data in the potential region in which the transition between dilute phase 1 and phase 4 of lithiated graphite occurs made it possible to determine independently the fraction of each of the two phases present as a function of potential, without relying on the coulometric information. The author also developed methods for the assembly and electrochemical characterization of Zn|MnO₂ and nickel metal-hydride (NiMH) alkaline batteries incorporating single microparticles of the active materials.

Voltage-time profiles for constant current operation for both types of devices were similar to those of commercially available batteries involving the same chemistries. The ability to monitor the state of charge of individual particles based strictly on spectroscopic data is expected to open new prospects for visualizing the flow of charge within electrodes in Li-ion batteries.

3. Experimental Considerations

The author also discusses some experimental considerations for studying single-particle electrodes and assembling single-particle batteries. Manipulation of the microparticles is critical, requiring the placement of μ -particles in contact with an electronic conducting support. Several strategies have been developed to manipulate μ -particles, including: A glass capillary attached to a syringe, which allows fragile particles to be captured by suction and then delivered to the substrate surface. A sharp spear of hard metal that can be inserted into a softer malleable material. A μ -disk electrode made out of a soft metal, into which hard particles can be embedded by applying pressure. The substrate should also exhibit a low and featureless capacitance within the potential range in which the charge storage material undergoes changes in redox state. Because of the small size of the materials involved, all manipulation and assembly operations must be performed under a microscope or telescope. Raman spectra were collected with a Raman 2000 system using a Verdi laser (532 nm) focused through an Olympus microscope as the excitation source. An all-glass, airtight, spectro-electrochemical cell was constructed for studies in nonaqueous electrolytes.

4. Single Microparticle Electrode Studies

The author also performed single microparticle electrode studies using both aqueous and non-aqueous systems.

4-1. Aqueous Systems

Nickel hydroxide is a charge storage cathode material for rechargeable batteries that power many hybrid vehicles. In its pristine form, this material consists of transparent spheres with diameters in the micrometer range. In situ measurements of the resistance of a single microparticle of spherical-Ni(OH)₂ were performed as a function of the state of

charge. Metallic zinc electrodes in Zn|MnO₂ batteries consist of particles tens of micrometers in characteristic dimensions dispersed in a concentrated aqueous KOH solution mixed with a polymer. In situ Raman spectra were recorded by inserting an electrochemically sharpened tungsten tip coated with a thin polymer layer into a single zinc particle harvested from a Zn/MnO₂ battery.

4-2. Nonaqueous Systems

The author's initial studies in nonaqueous electrolytes focused on the development of techniques for the electrochemical and Raman characterization of microparticles of lithiated transition metals oxides and carbonaceous materials, used as cathodes and anodes in commercial Li-ion batteries, in the absence of binders or conductivity enhancers. The strategy employed involved embedding a small number of μ -particles into gold for the cathodes and thermally softened nickel for the anodes, using high pressure. Nickel is suited for the study of anodes as it does not form alloys with lithium at room temperature.

5. Single Particle MicroRaman Spectro-electrochemistry

The author implemented methods to attach a single microparticle to the surface of a microelectrode, allowing for correlations between the current and the spectral features associated with that single microparticle. The results obtained for a single graphite microflake and for particles of LiMn₂O₄, both in polycrystalline and single crystal forms, are summarized in the article. Raman and electrochemical data for a single particle of KS-44, a commercially available graphitic powder, were in agreement with results reported by other groups using more conventional electrodes.

6. Single Particle Electrode Microbatteries

The same strategies developed for the manipulation of charge storage μ -particles were used to assemble single particle μ -batteries. Electrochemical tests were carried out by immersing the entire assembly

into a 9 M KOH solution. A performance assessment of commercial batteries usually involves applying a constant current to the battery while monitoring the potential across it. The rates of discharge are given in terms of C units, where 1C corresponds to a full discharge in one hour. Voltage versus time discharge curves were recorded for Zn|MnO₂ μ -batteries incorporating single particles of Zn and MnO₂. Charge-discharge curves for Ni|MH microbatteries were recorded at three different C rates. The data collected from these single particle μ -batteries closely mimic those found for technical devices. Single μ -particle LiMn₂O₄/carbon batteries were assembled by placing individual cathode and anode particles onto two isolated microelectrodes encased in a single glass rod, which was inserted into the cell filled with electrolytes. The self-discharge of the battery was monitored by measuring its potential as a function of time after the two microparticles in the battery had been fully charged independently. The potential was very stable for about 10 hours.

6. Concluding Remarks

These works aimed to develop methods of correlating the state of charge of battery microparticles with their spectroscopic characteristics, as a step toward monitoring the flow of charge within electrodes in actual operating batteries in real-time. The approach involves scanning the edge surface of an operating battery during charging and discharging using a Raman microscope. Further refinements will be required before the results of such experiments can be compared with theoretical models proposed in the literature to simulate the macroscopic behavior of actual devices.

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Advanced Energy Research Section

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1. Summary

The author spent the 2024 academic year (April 1, 2024 – March 31, 2025) as a Visiting Associate Professor, hosted by the Institute of Advanced Energy (IAE) within the Research Unit for the Realization of a Sustainable Society (RURSS), in collaboration with Professor Masato Katahira at his laboratory on the Uji Campus of Kyoto University.

In his report, the author presents recent developments in the efficient utilization of woody biomass.

2. Introduction

In pursuit of a sustainable future, we developed a biorefinery concept emphasizing environmental compatibility and process efficiency. In this approach, glycerol was employed as a green solvent to aid lignin decomposition during the initial biomass processing phase. Specifically, acid-catalyzed glycerolysis combined with microwave assistance was used to depolymerize lignin from sugarcane trash into antiviral compounds. These compounds significantly inhibited encephalomyocarditis virus (EMCV) replication in L929 cells without cytotoxic effects (1), as illustrated in Fig. 1.



Fig. 1. Integrated biorefinery of sugarcane trash producing antiviral lignin and bioethanol via acid-catalyzed glycerolysis, saccharification, and co-fermentation by two mixed engineered *S. cerevisiae* strains: glycerol- and xylose-fermenting yeasts.

To streamline processing and reduce associated costs, the resulting pulp was enzymatically hydrolyzed and subsequently fermented using a mixture of two metabolically engineered *Saccharomyces cerevisiae* strains: one capable of co-

fermenting glycerol and glucose (2), and the other capable of fermenting xylose (3). Together, these strains efficiently converted the released glucose, xylose, and glycerol into bioethanol, achieving a high titer of approximately 10%, as depicted in Fig. 1.

In collaboration with Professor Katahira's lab, a versatile peroxidase (VP) enzyme was introduced as an eco-friendly biocatalyst for lignin degradation. Its application significantly enhanced enzymatic hydrolysis, fermentation rates, and overall bioethanol yield (4), as shown in Fig. 2.

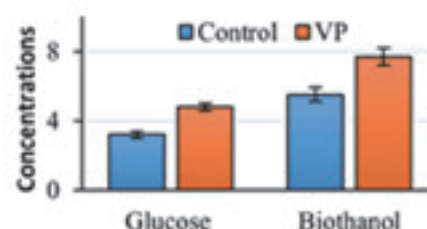


Fig. 2. Effect of versatile peroxidase (VP) treatment on glucose release during enzymatic hydrolysis and bioethanol production during fermentation, relative to control.

3. Results and achievements

(1). 2,3-butanediol production from glycerol

2,3-Butanediol (2,3-BDO) has attracted our attention due to its versatile applications as a bulk chemical. It serves as a precursor in the production of pharmaceuticals, cosmetics, synthetic rubber, inks, resins, perfumes, food additives, fuel additives, and even aviation fuel. Beyond industrial uses, 2,3-BDO also functions as an antifreeze agent, a plant growth stimulator, a drought resistance enhancer, and a biological control agent against plant pests and viruses.

We successfully redirected the native fermentation end product of baker's yeast from ethanol to 2,3-butanediol through metabolic engineering of the fermentation pathway, using glycerol as the main substrate, as depicted in Fig. 3. This represents the first study to demonstrate the conversion of glycerol to 2,3-butanediol by baker's yeast (5).

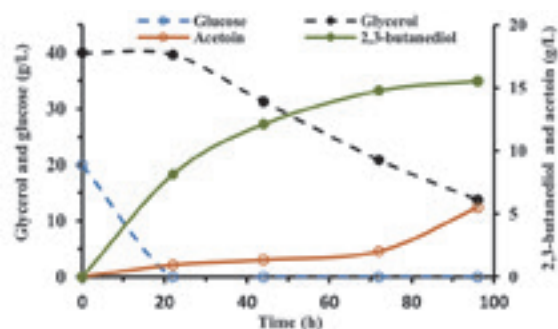


Fig. 3. Time-course profiles of glycerol and glucose consumption and production of 2,3-butanediol and acetoin during fermentation by engineered *S. cerevisiae*.

(2). A novel acetic acid co-utilization strategy during fermentation of glucose

Acetic acid, a byproduct of glucose fermentation, represents over 2% of the glucose consumed by our baker's yeast strain (**Fig. 4**). In second-generation bioethanol production from lignocellulosic biomass, additional acetic acid released during biomass decomposition may further hinder fermentation, as also seen in **Fig. 4**. To address this, we engineered a yeast strain that increases ethanol production rate by over 3.4-fold and enables acetic acid co-utilization. The strain performs well under low-oxygen conditions and shows ethanol-induced flocculation, aiding downstream recovery (6). The enhanced performance is demonstrated in **Fig. 4**.

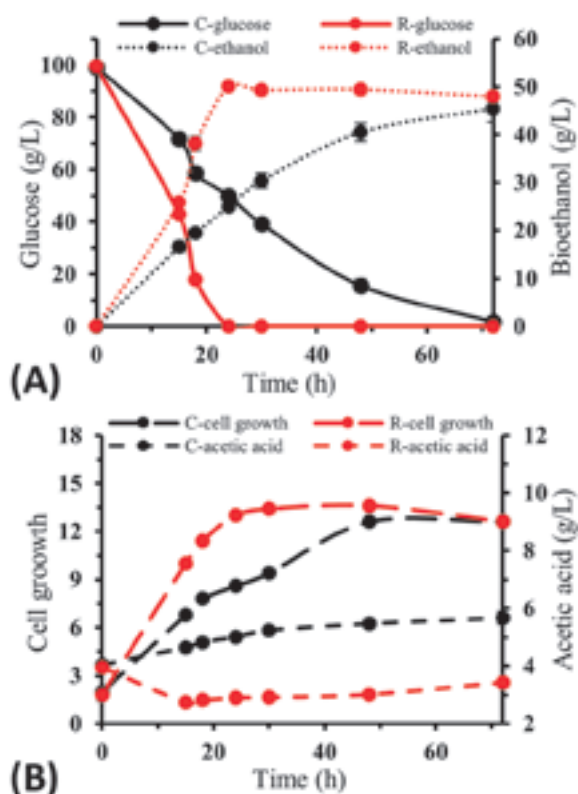


Fig. 4. Glucose fermentation and acetic acid co-utilization by control (C) and recombinant (R) *S. cerevisiae* strains. (A) Glucose consumption and ethanol production. (B) Cell growth and acetic acid utilization. The recombinant strain shows faster glucose depletion, higher ethanol yield, improved growth, and active acetic acid consumption.

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Advanced Energy Research Section

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1. Summary

The author spent one and half months at Kyoto University, Uji Campus in Prof. Nohira group. A review of the most promising technologies for electrochemical reduction of CO₂ for carbon negative technologies is presented. Recent efforts to convert CO₂ into valuable carbon materials using molten salt electrolysis are summarized and discussed here.

2. Introduction

In order to achieve carbon neutrality by 2050, it is necessary to not only capture and store carbon dioxide (CO₂) emissions (Carbon dioxide Capture and Storage; CCS), but also to capture and effectively utilize CO₂ (Carbon dioxide Capture and Utilization; CCU). Electrochemical conversion of CO₂ to carbon using molten salts is considered to be one of the most promising CCU technologies, and is attracting attention [1]. Several research groups have reported the electrodeposition of various carbon allotropes, such as graphite [2] and carbon nanotubes [3]. Prof. Nohira's group has reported that they obtained diamond and amorphous carbon [4]. This study summarizes the use of molten salt electrolysis for the synthesis of high-value-added carbon materials such as graphite from carbon dioxide.

3. Electrochemical approaches and their challenges

Methods for breaking down CO₂ into other carbon-containing substances include the reduction of CO₂ by electrolysis or photoelectrolysis in aqueous solutions [5-7]. One of the advantages of this process is that it can produce a variety of products, including alcohols, aldehydes, carboxylic acids, CO, and even hydrocarbons. These substances are important raw materials in the chemical industry, and it is beneficial to be able to synthesize such chemicals from carbon dioxide. Furthermore, this process can also be seen as an energy storage process that converts electrical and light energy into chemical energy. The fact that it can produce many different types of products can also be a disadvantage. The fact that it can produce many different types of products can also be a disadvantage. It is difficult to improve the selectivity of the desired products and maximize

the yield. Since most of the products remain in aqueous solution, it is always difficult to separate them efficiently and economically. The low solubility of CO₂ gas in water is also a problem. Furthermore, the greatest challenge is the presence of water as a solvent. The decomposition reaction of water is thermodynamically and kinetically more favorable than the CO₂ reduction reaction, so it leads to the generation of hydrogen rather than the formation of the desired substance.

4. Molten salts as promising electrolytes

Inorganic molten salts are promising for CO₂ electrolysis due to high CO₂ solubility, stability, and wide potential windows, with high temperatures aiding kinetically challenging C=O bond breaking. This can enable cost-effective electrode materials and the direct splitting of CO₂ into valuable carbon and oxygen. Despite its potential for carbon material production and environmental benefits, this method has been overlooked, partly due to existing carbon sources and process understanding. However, the growing demand for sustainable carbon material synthesis has renewed interest in molten salt CO₂ electrolysis as a key technology. Research is focusing on various molten salt systems like Li₂CO₃ and CaCl₂-based electrolytes to control the resulting carbon materials, with CaCl₂-based salts offering advantages in stability, oxide solubility, and cost-effectiveness, despite requiring further investigation compared to other systems. LiCl-KCl, a long-established representative alkali metal chloride molten salt, is also promising.

5. Various carbon materials obtained by molten salt electrolysis

Early research in the 2000s explored carbon film deposition from molten carbonates, yielding mostly amorphous films controlled by carbonate ion diffusion. Hsu et al. previously reported CNT formation in molten LiCl via lithium intercalation of a graphite cathode, not CO₂ electrolysis [8]. Electrolytic CO production was also investigated using Ti cathodes in Li₂CO₃ and stainless steel in CaCl₂-CaO, with high CO₂ favoring CO evolution. Ren et al. later achieved controlled CNF production directly from CO₂ in molten carbonates with metal additives acting as nucleation sites [9]. Metal encapsulation in carbon nanostructures, like Ge in

CNTs, was also demonstrated using molten salt electrolysis. Furthermore, graphene sheets were produced from CO₂ in CaCl₂-based melts, attributed to catalytic effects and CO microexplosions. Nanodiamonds were synthesized in LiCl with moisture and CO₂ injection, involving graphite exfoliation and a nanoreactor mechanism. Carbon nanospheres with unique morphologies were obtained from molten LiCl-KCl-CCO₃, likely influenced by CO bubbles. Other carbon nanomaterials like nano-onions and 3D graphene scaffolds have also been synthesized via CO₂ electro-splitting in molten salts.

6. Reaction mechanism

While the synthesis of diverse carbon materials via CO₂ electro-splitting in molten salts under varying conditions has been demonstrated, research focusing on the underlying reaction mechanisms and detailed cathodic behavior remains scarce. Ito et al. explored the carbonate reduction and re-oxidation processes in LiCl-KCl melt [10], proposing a two-step electrochemical reduction mechanism. Using chronopotentiometry, they estimated the diffusion coefficient of carbonate ions at 450°C, and the activation energy was determined from the Arrhenius plot. Ge et al. investigated the carbon nucleation process in LiCl-Li₂CO₃ molten salt, primarily using SEM analysis of electrolysis products [11]. Through short-term electrolysis under different conditions, they revealed that the morphology of the resulting carbon materials is influenced by both the substrate and the applied cell voltage.

7. Inert anodes

Inert anodes for CO₂ electrolysis in molten salts, categorized as metals, alloys, and oxides, each present distinct advantages and disadvantages. Metals and alloys generally offer superior physicochemical properties like electrical conductivity and mechanical strength but often suffer from poor stability, especially in halide molten salts, and some, like Ir or Pt, are cost-prohibitive compared to oxides. Given the significance of halides as electrolytes, developing stable oxide inert anodes is crucial. SnO₂ has shown relative stability in corrosive molten salt environments; however, its inherent physical limitations necessitate the use of additives like CuO and Sb₂O₃ for electrode applications. SnO₂-based electrodes have demonstrated reasonable inertness in various molten carbonate and chloride systems. Despite their accepted stability, their conductivity and mechanical strength remain inferior to metals. Furthermore, the formation of a poorly conductive

CaSnO₃ layer on SnO₂ electrodes in CaO-containing melts and its potential reduction by alkali/alkaline earth metals leading to electrode consumption pose additional challenges. To overcome these limitations, recent efforts have focused on developing composite oxide materials such as CaRuO₃, CaTi_{1-x}Ru_xO₃, and TiO₂·RuO₂ inert anodes. While the high cost of Ru compared to SnO₂ is a significant drawback, these composite oxides have exhibited improved conductivity and commendable stability in both molten chloride and carbonate salts.

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