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# Unique Reaction Environment within the Electrical Double Layer for Electrocatalysis

전기촉매반응을 위한 전기이중층 내의 고유한 반응 환경

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Graduate School of Seoul National University Department of Chemistry Electroanalytical Major

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- Preconcentration and Marcus-Hush-Chidsey Theory -

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### Abstract

# Unique Reaction Environment within the Electrical Double Layer for Electrocatalysis

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Since the electrical double layer (EDL) is where heterogeneous electron transfer occurs, understanding the effects of the electrode-electrolyte interface structure on electrocatalysis is important. The strong electric field ( $\sim 10^9$  V/m) in the EDL offers unique environment for electrochemical reactions by altering the solvation structure and mass transport of redox species. This EDL structure can be the key to complementing the electrocatalyst designing principle which mostly depends on the Sabatier principle alone (**Chapter 1**). Yet, it is challenging to evaluate the physicochemical properties within EDL.

This thesis corroborates the EDL structure to describe the electrocatalytic activity according to the electrode material, as exemplified in the hydrogen evolution reaction (HER) in an acidic aqueous solution and the bromine reduction reaction in a polybromide ionic liquid. Additionally, it introduces methodologies to evaluate two important properties of the EDL structure: the potential of zero charge (PZC) of electrodes and the reorganization energy. **Chapter 2** introduces the methodology to measure the local PZC of electrodes using the scanning electrochemical cell

microscopy (SECCM). Applying the SECCM to the high-entropy alloy material library (HEA-ML) revealed that the PZC of the HEA is directly correlated to its elemental composition-weighted average work function and that the HER activity in an acidic electrolyte favors a strong negative electric field in the EDL. **Chapter 3** describes the methodology to measure the reorganization energy of the bromine reduction in a polybromide ionic liquid based on the Marcus-Hush-Chidsey electron transfer kinetics theory. Reorganization energy on the platinum surfaces modified with titanium oxide of positive charges suggested the surface-charge dependent solvation structure in the inner Helmholtz plane (IHP), which affects the electron transfer kinetics. **Chapter 4** reports a method to evaluate the reorganization energy of the polybromide ionic liquid using the SECCM. This enables the investigation of the reorganization energy on alloys, which are difficult to fabricate into ultramicroelectrodes. **Chapter 5** summarizes the dissertation and addresses a future perspective on the EDL engineering as a promising electrocatalyst designing principle.

**Keywords :** Electric double layer (EDL), Potential of zero charge (PZC), Reorganization energy, Scanning Electrochemical Cell Microscopy (SECCM), High-entropy alloy (HEA)

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# Abbreviations

AIMD	Ab initio molecular dynamics
APT	Atomic Probe Tomography
BV kinetics	Butler-Volmer kinetics
CV	Cyclic voltammetry
DFT	Density functional theory
DOS	Density of states
ECSA	Electrochemically active surface area
EDL	Electrical double layer
EDX (EDS)	Energy-dispersive X-ray analysis
EIS	Electrochemical impedance spectroscopy
Estimated WF	Elemental composition-weighted average work function
ET	Electron transfer
HEA	High-entropy alloy
HEA-ML	High-entropy alloy material library
HER	Hydrogen evolution reaction
HOR	Hydrogen oxidation reaction
$H_{upd}$	Hydrogen underpotential deposition
IHP	Inner Helmholtz plane
IL	Ionic liquid
MA	Measurement area
$MBPBr_{2n+1} \\$	1-butyl-1-methylpyrrolidinium polybromide
MEPBr	1-ethyl-1-methylpyrrolidinium bromide

$MEPBr_{2n+1} \\$	1-ethyl-1-methylpyrrolidinium polybromide
MH model	Marcus-Hush model
MHC model	Marcus-Hush-Chidsey model
MT	Mass transport
OER	Oxygen evolution reaction
OHP	Outer Helmholtz plane
ORR	Oxygen reduction reaction
PME	Potential of maximum entropy
PZC	Potential of zero charge
Rds	Rate-determining step
RHE	Reversible hydrogen electrode
RT-IL	Room-temperature ionic liquid
SECCM	Scanning electrochemical cell microscopy
SEM	Scanning electron microscope
SHE	Standard hydrogen electrode
UME	Ultramicroelectrode
WF	Work function
XRD	X-ray diffraction

## **Chapter 1. General Introduction**

# **1.1.** The Sabatier Principle: To Predict and Explain the Electrocatalytic Activities of a Given Electrode

Finding the descriptor for electrocatalytic activities is of great concern in electrochemistry in view of understanding the origin of activities of electrocatalysts and enabling the efficient design of electrocatalysts with high activities. The most widely accepted theory for the activity descriptor is the Sabatier principle that the heterogeneous catalytic rate can be maximized when the interaction between the electrode and the reaction intermediate is intermediate. Too strong binding obstructs the desorption of the product from the surface while too weak binding impedes the adsorption of the reactant to the surface. The principle can be represented as the volcano plot demonstrating reaction rates or electrocatalytic activities as a function of binding strength of intermediates. For example, hydride binding energy<sup>[1]</sup> and adsorption energy of \*OH and \*O<sup>[2]</sup> have been the descriptor for the activity trends of the hydrogen evolution reaction (HER) and the oxygen reduction reaction (ORR), respectively. Indeed, the Sabatier principle have been successfully utilized to design the electrocatalysts of not only pure metal electrodes<sup>[1]</sup> but also metal oxide electrodes,<sup>[3]</sup> single-atom electrocatalysts,<sup>[4]</sup> and high-entropy alloy (HEA) <sup>[5]</sup> for the HER,<sup>[6]</sup> the oxygen evolution reaction (OER),<sup>[3]</sup> H<sub>2</sub>O<sub>2</sub> production<sup>[7]</sup> and etc.

### **1.2.** Limitations of the Sabatier Principle

In spite of the successful utility of the Sabatier principle, it alone cannot explain all the experimental data. First, evaluating the binding energy of intermediates necessitates computational techniques such as density functional theory (DFT).<sup>[8]</sup> The calculated binding energy values often lack of information about experimental factors that cannot be considered in the computation due to technical limitations. Especially, the heterogeneous electron transfers occur at the electrode-electrolyte interface where the electrical double layer (EDL) is present. The EDL offers unique reaction environment for electrochemical reactions different from the bulk space. This includes the strong electrical field in the EDL and the enrichment of cations and anions in response to the surface charge of the electrode. The interfacial electric field with a strength of ca. 1 V/nm constrain the preferred orientation of molecules,<sup>[9]</sup> and reduce the dielectric constant of solvent molecules through dielectric saturation.<sup>[10]</sup> The supporting cations can stabilize the reaction intermediate and offer local acidity and electric field.<sup>[11,12]</sup> Ab initio molecular dynamics (AIMD) has been employed to compute the dynamics of molecular movements in response to local electric field, but it can compute only several hundreds of molecules because of the dramatic increase of the computational coasts. This number of molecules is even not enough to compute the electrolyte at a concentration not less than 0.01 M.<sup>[13]</sup>

Secondly, the Sabatier principle predicts the catalytic activities based on the thermodynamics, and it tends to oversimplify kinetic factors. The design of a high activity electrocatalyst based on the Sabatier principle involves calculating the Gibbs free energy of reactants, intermediates, and products, and identifying materials with the least difference in free energy along the reaction coordinate.<sup>[8]</sup> This analogizes

linear Gibbs energy relation that describes the reaction rate in relation to the thermodynamic driving force. Conversely, there has been growing attention on the interfacial microscopic structure of redox species affecting electron transfer kinetics to explain electrocatalytic activity trends. This includes the solvation structure for redox species,<sup>[14–16]</sup> rigidity of the solvent molecules,<sup>[17,18]</sup> hydrogen bonding network in the EDL.<sup>[19]</sup>

Finally, few studies have addressed the experimental method to estimate the binding energy.<sup>[20,21]</sup>

### **1.3.** Mass Transport in the Electrical Double Layer

In electrochemistry, the current is primarily influenced by electron transfer occurring at the electrode-electrolyte interface and the mass transport of redox species within the electrolyte. In most electrocatalysis systems, the operating conditions involve overpotentials that are adequate for the electron transfer rate to exceed the mass transport flux. Therefore, modulating the mass transport has been one of strategies to boost electrocatalytic current.

The transport of chemical species in a solution takes place through diffusion, migration, and convection. Diffusion governs the majority of voltammetric behaviors, with its flux being determined by the concentration gradient of chemical species. Convection become significant in hydrodynamic systems, such as rotating disk electrodes and electrochemical cells that involve fluid flow. On the other hand, migration represents the movement of charged species in response to an electric field. Therefore, the interfacial electric field of the EDL has a critical impact on the mass transport of redox species, giving rise to enrichment or depletion of redox species at the interface.

Ions can undergo preconcentration at the interface to compensate for excess charges on an electrode surface. The magnitude of the excess surface charge on the electrode surface is determined by the potential of zero charge (PZC), which refers to the potential at which no excess charge exists on the electrode surface. Consequently, when the electrode potential exceeds its PZC, ions with positive charges become enriched on the electrode surface, whereas ions with negative charges become enriched when the electrode potential is lower than its PZC. This preconcentration effect has been utilized to facilitate a target reaction or to impede a side reaction. For example, J. Wordsworth *et al.* reported mesoporous Pt-Ni nanoparticles as an ORR electrocatalyst in 0.1 M HClO<sub>4</sub>.<sup>[22]</sup> Since the operating potential for ORR is lower than the PZC of the electrocatalyst, H<sup>+</sup> should be accumulated in the interface. The increased interfacial H<sup>+</sup> concentration at the Pt-Ni catalyst with smaller channers induced increased ORR activity until the potential reached O<sub>2</sub> mass transport limited region. Moreover, adding alkali metal ion such as K<sup>+</sup> in a strong acidic electrolyte hinders the HER, which is the side reaction of CO<sub>2</sub> reduction.<sup>[23]</sup> This is because K<sup>+</sup> occupies the inner Helmholtz plane (IHP) instead of H<sup>+</sup> to compensate for the negative charge on the electrode, thus the interfacial concentration of H<sup>+</sup>, a reactant of HER, is reduced.

#### **1.4.** Microscopic Electron Transfer Kinetics Theory

The Butler-Volmer (BV) kinetics, the most widely applied empirical kinetics model for heterogeneous electron transfer, estimates the rate constant for electron transfer following the free energy relationship. Equation (1-1) and (1-2) represent the activation energy for reduction ( $\Delta G_c^{\ddagger}$ ) and oxidation ( $\Delta G_a^{\ddagger}$ ) in the BV model, respectively, assuming the linear free energy curve along the reaction coordinate.

$$\Delta G_c^{\ddagger} = \Delta G_{0c}^{\ddagger} + \alpha F(E - E^0) \tag{1-1}$$

$$\Delta G_a^{\ddagger} = \Delta G_{0a}^{\ddagger} + (1 - \alpha) F(E - E^0)$$
(1-2)

Here,  $\Delta G_{0c}^{\dagger}$  and  $\Delta G_{0a}^{\dagger}$  are respectively the activation energy for reduction and oxidation at the standard potential ( $E^{0}$ ),  $\alpha$  is the transfer coefficient representing the asymmetry of the free energy curve at the transition state, F is the Faraday constant, and E is the electrode potential. The BV model accounts the dependency of the activation energy on the overpotential ( $\eta = E - E^{0}$ ), but lacks of the explanation for the intrinsic activation energy at the standard potential. Moreover, it fails to offer any prediction of the kinetic factors based on the microscopic structures of redox species, solvation structure and interfacial physicochemical properties.

On the other hand, the Marcus theory for the microscopic electron transfer kinetics proposes the reorganization energy ( $\lambda$ ) as a factor determining the activation barrier:

$$\Delta G_c^{\ddagger} = \frac{\lambda}{4} \left( 1 + \frac{F(E - E^0)}{\lambda} \right)^2 \tag{1-3}$$

 $\lambda$  is the energy required for the reactant to have the product geometry. Structural changes of both the redox species (inner-sphere reorganization energy,  $\lambda_i$ ) and solvation shell (outer-sphere reorganization energy,  $\lambda_o$ ) during electron transfer

contribute to the  $\lambda$  (Equation (1-4)).

$$\lambda = \lambda_i + \lambda_o \tag{1-4}$$

According to the Born model of solvation, the  $\lambda_0$  for heterogeneous electron transfer can be described by Equation (1-5).

$$\lambda_o = \frac{e^2}{8\pi\varepsilon_0} \left(\frac{1}{d_o} - \frac{1}{d_R}\right) \left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right)$$
(1-5)

Where *e* is the elementary charge,  $\varepsilon_0$  is the vacuum permittivity,  $a_o$  is the radius of the solvated redox species,  $d_R$  is twice the distance from the center of the molecule to the electrode surface, and  $\varepsilon_{op}$  and  $\varepsilon_s$  are the optical and static dielectric constant of solvents, respectively. This implies that manipulating the solvation structure can be crucial for controlling the rate for electron transfer. The Marcus theory for the heterogeneous electron transfer kinetics is the Marcus-Hush-Chidsey (MHC) model, which will be discussed in the **Chapter 3.** Indeed, the MHC model has been successfully applied to explain the solvation effects on not only the simple outer-sphere reaction,<sup>[15]</sup> but also deposition,<sup>[14]</sup> intercalation,<sup>[24]</sup> and innersphere reactions.<sup>[16,25]</sup>

Within the EDL, the presence of a strong electric field gives rise to distinct structural characteristics in the solvent. First, the strong electric field restricts the polarization modes of solvent molecules, leading to a reduction in the solvent's static dielectric constant. This phenomenon is known as dielectric saturation. As described by Equation 1.5, the decrease in  $\varepsilon_s$  corresponds to a decrease in the reorganization energy, which facilitates the electron transfer kinetics. This has been exemplified in the enhanced kinetics of homogeneous electron transfer between molecules in the EDL.<sup>[26]</sup> Secondly, the accumulated spectator cations in the EDL can modify the solvation structure. The cation effects on the HER have emerged as recent and trending topics in electrocatalysis. For example, the strongly hydrated cations, Li<sup>+</sup>, promotes the alkaline HER. This has been attributed to the stabilization of surface OH adaptom species<sup>[27]</sup> or reduced  $\varepsilon_s$  of surrounding solvent molecules dielectric constant of through noncovalent interactions.<sup>[16]</sup>

#### **1.5.** Aims of Thesis

In conclusion, while the Sabatier principle successfully explains the trends in catalytic activity based on electrode materials, the design of electrocatalysts with high activity heavily relies on screening and trial and error, which demands extensive experimentation. This issue may stem from the limitations of the incomplete knowledge about the designing principle, as discussed in section 1.2. Therefore, there has been a continuous demand for fundamental studies, especially about interfacial structure and kinetics, to bridge the gap between the activity descriptor model and the actual phenomena. However, the two-dimensional surface nature of the interface hampers its study. The interface signal tends to be weak, and to be buried in signals from the three-dimensional space bulk, and therefore the significance of the interface is likely to be underestimated in explaining electrocatalysis due to the difficulty of exploring it.

This thesis is concerned with probing the physicochemical properties within the EDL and elucidating the role of the interfacial reaction environment on electrocatalysis in aqueous solution and room temperature ionic liquids (RT-ILs). Herein, two properties of the EDL are discussed: the PZC of electrodes and the reorganization energy.

In **Chapter 2.** a scanning electrochemical cell microscopy (SECCM) enabled high spatial measurements of PZCs on complex alloy electrodes as well as single material electrodes. High-throughput experimentation with SECCM and a HEA material library (HEA-ML) reveals increased HER activity on the HEA surface with more positive PZC, which can be attributed to the preconcentration of H<sup>+</sup> at the interface due to the stronger negative electric field in the EDL.

**Chapter 3.** describes the method to evaluate reorganization energy within the EDL of RT-ILs based on the MHC model for electron transfer kinetics using a polybromide RT-IL as a model system. Through reorganization energy, the surface charge-dependent solvation structure of the IHP in the RT-IL is explored.

In **Chapter 4.**, the SECCM is utilized to expand the application of the range of electrode material candidates capable of measuring reorganization energy in the RT-IL.

**Chapter 5.** provides a comprehensive summary of the dissertation and the future perspective on studying interfacial structure to complement the electrocatalyst designing principle.

# Chapter 2. Acidic Hydrogen Evolution Reaction Activities in High-entropy Alloys Correlates with its Composition Dependent Potential of Zero Charge

Here we suggest the PZC as a potential descriptor for HER activities in perchloric acid solution, which was further supported by the finite element simulation. The dependency of PZC of HEAs on elemental composition was identified by high-throughput experimentations with a HEA-ML and the SECCM.

This chapter consists of a communication currently in preparation. I was responsible for the experimentation, data analysis, simulation and paper preparation. Emmanuel B. Tetteh designed the experiments and carried out some of electrochemical experiments. Some data appear in his thesis, which has been reanalyzed in this chapter. Alan Savan, Bin Xiao, and Olga A. Krysiak synthesized and characterized the HEA-ML. T. H. Piotrowiak performed XRD analysis of the electrodes. Wolfgang Schuhmann, Taek Dong Chung and I conceived the project, and this work was supervised by Wolfgang Schuhmann, Taek Dong Chung, Alfred Ludwig, and C. Andronescu.

# Acidic Hydrogen Evolution Reaction Activities in High-entropy Alloys Correlates with its Composition Dependent Potential of Zero Charge

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### 2.1. Abstract

The vast possibilities in the elemental combinations of HEAs make it essential to discover activity descriptors for establishing rational electrocatalyst design principles. Despite the increasing attention on the PZC of HER electrocatalyst, neither the PZC of HEAs nor the impact of the PZC on the HER activity at HEAs has been described. Here, we use SECCM to determine the PZC and the HER activities of various elemental compositions of a Pt-Pd-Ru-Ir-Ag thin-film HEA-ML with high statistical reliability. Interestingly, the PZC of Pt-Pd-Ru-Ir-Ag is linearly correlated with its composition-weighted average work function. The HER current density in acidic media positively correlates with the PZC, which can be explained by the preconcentration of H<sup>+</sup> in the electrical double layer.

Keywords : Hydrogen evolution reaction (HER) • High-entropy alloy (HEA) •
Potential of zero charge (PZC) • Scanning electrochemical cell microscopy (SECCM)
High-throughput analysis

#### 2.2. Introduction

HEAs are attractive electrocatalysts for reactions such as the HER,<sup>[28,29]</sup> the ORR,<sup>[30–32]</sup> the OER<sup>[33,34]</sup> and alcohol oxidation reactions.<sup>[35,36]</sup> The electronic interactions between different neighboring atoms and strain effects caused by the different sizes of the atoms in a HEA create unique active sites distinguished from those of the principal elements. Moreover, the proximity of active sites with different binding energies offers a route to break scaling relations in electrocatalysis by the sequential stabilization of different intermediates.<sup>[37]</sup> Since the electrocatalytic activities of HEAs are influenced by the constituent elements and their ratios, it is essential to understand the fundamental relationship between electrocatalytic activities and composition to speed up HEA electrocatalyst design.

Classically, the binding strength of intermediates has been considered the most critical descriptor for electrocatalytic activities according to the Sabatier principle; however, electrochemical interfacial properties such as the PZC and the EDL structure at the electrode-electrolyte interface have gained considerable interest for understanding the activity<sup>[38,39]</sup> and selectivity<sup>[40,41]</sup> of electrocatalysts. For the HER in alkaline media, the interfacial water and hydrogen network structure in the EDL plays a bigger role concerning the HER kinetics than the hydrogen binding energy—the sluggish HER kinetics in the electrode with strong negative electric field.<sup>[18,19]</sup> However, L. Rebollar *et al.* reported that the kinetic isotope effect of acidic HER was 1 when the hydrogen in the electrolytes was substituted by deuterium while that of alkaline HER was higher than 1.5.<sup>[42]</sup> This suggests that the effect of the PZC as well as the role of the EDL structure on acidic HER may be completely different from that in alkaline electrolytes. Hence, identifying the effect of PZC on HER

electrocatalysts in acidic media is important for their rational design. In particular, considering the growing use of alloys as HER electrocatalysts, the relationship between the PZC and the acidic HER activity in alloy-type electrodes including HEAs needs to be clarified. Until now, neither the PZC of HEAs nor experimental strategies to determine the PZC of a HEA have been implemented.

Commonly the PZC of an electrode is derived from double layer capacitance  $(C_{dl})$  measurements using cyclic voltammetry (CV) <sup>[43,44]</sup> and electrochemical impedance spectroscopy (EIS),<sup>[45]</sup> as well as CO displacement techniques.<sup>[46]</sup> These methods were successfully applied to determine the PZC and revealed the double layer structure at single crystalline electrodes such as Pt(111)<sup>[43,44,47]</sup> and Au(111).<sup>[47,48]</sup> However, for HEA surfaces, the potentials of the double layer regions of the principal elements overlap, and CVs may be accompanied by phase transitions of the alloys as can be seen in the corresponding Pourbaix diagrams. This makes it elusive to accurately evaluate  $C_{dl}$ . Furthermore, the conventional methods provide a single data value for one macroscopic electrode which makes it challenging to obtain a sufficiently high data reliability. Considering the wide variation in composition space offered by HEAs, high-throughput experimentation is necessary to elucidate phenomena related to HEA electrocatalysis.<sup>[49]</sup> SECCM has enabled the exploration of the structure-activity correlation through robust, versatile, and high-throughput measurements with high spatial resolution.<sup>[50–52]</sup> Recently, Wang *et al.* presented a method to measure the local PZC of polycrystalline Pt and Au using SECCM.<sup>[53]</sup> This method combines SECCM and the immersion technique<sup>[54]</sup> for PZC measurement, evaluating the potentialdependent excess charges in the EDL. The hopping mode of SECCM automatically performs multiple independent measurements at a new clean electrode surface,
providing statistically reliable data as well as spatial resolution.

We investigate for the first time the PZCs of different HEA compositions using an improved SECCM protocol and a noble-metal-based thin-film HEA-ML, and further explore the relationship between the measured PZC and the composition of the HEA-ML as well as its effects on the HER electrocatalysis at the HEA surfaces. The method for measuring the PZC by SECCM was adapted from<sup>[53]</sup> with two important modifications: (1) the implementation of the charging current fitting to estimate the time constant of the formed micrometric electrochemical cell upon droplet contact which depends on the electrode area, the nature of the electrolyte solution, and the electrode material; and (2) the implementation of initial surfacecleaning voltammetry enabling reliable PZC measurements on complex materials. Screening PZCs of the HEA-ML by SECCM revealed a simple parameter to predict the PZC of the HEA-ML based on its composition: an estimated work function (WF) which by itself is a composition-weighted average of the WF of each constituent element. HER activities measured for the different HEA compositions were positively correlated to the measured PZC in acidic electrolyte, which can be explained by the electric field-induced preconcentration of H<sup>+</sup> in the electrolyte-HEA interface.

1 6

# 2.3. Experimental Methods

#### 2.3.1. Materials

Perchloric acid (HClO<sub>4</sub>) and potassium chloride (KCl) were purchased from Sigma-Aldrich. All chemicals were used as supplied. All solutions were prepared with Milli-Q deionized water. Single barrel quartz capillaries, 0.9 mm inner and 1.2 mm outer diameter and 10 cm length with filaments were purchased from Sutter instrument.

#### 2.3.2. Electrode Preparation

All elements of the HEA-ML were simultaneously deposited on a 100 mm diameter single crystal (100) Si wafer with 1000 nm wet thermal SiO<sub>2</sub> as a barrier layer against substrate reactions by combinatorial magnetron sputtering (DCA Instruments, Turku Finland) using five metallic targets: Ag (purity 99.99%), Ir (purity 99.99%), Pd (purity 99.99%), Pt (purity 99.99%), and Ru (purity 99.95%). Each target was oriented at an angle of 45° to the fixed sample located at the confocal point, giving a target-to-substrate distance of 18.5 cm. The five cathodes are equally spaced in a circle (72° apart), with this geometry resulting in nearly linear thickness gradients from each. The deposition process started from a base vacuum of 2 x 10<sup>-6</sup> Pa at 25° C and was done without additional intentional heating. All targets were precleaned immediately before the film was deposited against individual closed shutters. Depositions were done in Ar (99.9999%) at a pressure regulated to 0.67 Pa. The power applied to each target was adjusted to yield the desired alloy composition at the substrate center, and the total deposition rate at that point was 0.3 nm/s. The polycrystalline Pt thin-film electrode was prepared using the same method for the HEA-ML fabrication with the

Pt target which was not tilted. 20 nm Ti and 40 nm Pt were deposited on the Si wafer in sequence. The polycrystalline Au thin-film electrode was prepared using (100) Si wafer (Wacker) coated sequentially with Ti and Au by vapor deposition in a metal vaporization setup (Leybold, Germany). The elemental composition of the prepared HEA-ML was determined by energy-dispersive X-ray analysis (EDX) with an acceleration voltage of 20 kV using a scanning electron microscope (SEM, JEOL 5800) and a silicon-drift detector (INCA Xact, Oxford Instruments).

#### 2.3.3. SECCM Tip Preparation

After carefully cleaning a single barrel quartz capillary with wipes soaked in isopropanol, it was placed in a laser puller (Sutter instrument). It was pulled with the puller parameters of HEAT 600, FIL 4, VEL 40, DEL 130, PUL 104-120. The diameter of the tip was measured by SEM (FEI Quanta 3D). Only tips having diameters of about 1 µm were used for further SECCM experiments (**Figure 2-1a**). After filling the capillary with electrolyte 10 mM HClO<sub>4</sub> solution, the wider end of the single barrel SECCM tip was attached to an Eppendorf tip, of which the ending was slightly cut (**Figure 2-1b**). A Ag/AgCl (3 M KCl) reference electrode was used, and the potential of the reference electrode was calibrated before and after electrochemical experiments.

#### 2.3.4. SECCM Instrumental Set-up

All electrochemical experiments were conducted using a home-built SECCM.<sup>[55]</sup> The SECCM was controlled by FPGA card (PCIe-7852R) and a LabVIEW (National Instruments) software that was modified based on the Warwick Electrochemical Scanning Probe Microscopy (WEC-SPM) toolbox. SECCM was installed on a

vibration-damping table (RS 2000, Newport) with four S-2000 stabilizer legs (Newport). A single barrel SECCM tip and an electrode were mounted on a pipette holder and a sample holder, respectively. The pipette holder was kept stationary while the sample holder was coarsely moved by x,y,z-stepper motors (Owis) with a LStep PCIe (Lang) controller, and was finely controlled by a x,y,z-piezo cube (P-611.3S nanocube, Physik Instrumente) with an analog amplifier (E-664, Physik Instrumente). First, using the stepper motors, an optical camera (DMK 21AU04, The Imaging Source) and a cold light source (KL1500 LCD, Schott), the SECCM tip was carefully placed about 20-50 µm above an interested region of an electrode surface. Then, the tip was approached to the surface by movement of the z-piezo, and the lateral position of the tip during scan-hopping experiments was controlled by the x,ypiezos. The electrochemical cell was a 2-electrode system, with the part of the electrode surface contacting the droplet as working electrode, and the Ag/AgCl (3 M KCl) reference electrode/counter electrode inserted into the Eppendorf tip from above. The current flowing through the reference electrode was measured using a variable gain transimpedance amplifier (DLPCA-200, FEMTO Messtechnik) and a variable gain voltage amplifier (DLPVA-100-B-S, FEMTO Messtechnik). The data was acquired with a rate of one data point per 4096 µs. All electrochemical experiments were conducted under Ar atmosphere to avoid any interference caused by  $O_2$ .



**Figure 2-1.** (a) Typical SEM image of the glass microcapillary opening used as the scanning electrochemical cell microscopy (SECCM) tip with a diameter of about 1.1  $\mu$ m. (b) The schematic illustration of the electrochemical cell used in the SECCM. A SECCM tip is fixed to the tip holder, and the electrode is put in the Petri dish set on the piezo. A constant flow of Ar is introduced using the tube connected to the Petri dish during the SECCM measurements, and the SECCM tip is placed in a hole with a diameter of several centimeters in the lid of the Petri dish. The bigger end of the SECCM tip was elongated with an Eppendorf pipette tip in order to put the Ag/AgCl (3 M KCl) reference electrode into the electrolyte.

#### 2.3.5. Potential of Zero Charge Determination

The SECCM tip was approached to the electrode surface with a z-velocity of 0.5  $\mu$ m/s until the current was higher than the positive threshold or lower than the negative threshold, signaling that the droplet of the tip touched the electrode surface. The positive and negative thresholds were usually set to about 0.2 pA higher and lower than the background noise, respectively. As demonstrated in **Figure 2-2**, the PZC measurement method consists of an initial approach of the tip to the sample surface, surface-cleaning CV, and the PZC measurement protocol. CVs were performed for at least 4 cycles with a potential range including the hydrogen underpotential adsorption region and the metal oxide formation region with a scan rate of 1 V/s. During the PZC measurement protocol, the tip was repetitively approached to the same position of the surface at a series of varying sample potentials.



**Figure 2-2.** (a) Schematic illustration of the SECCM set-up, and the operation scheme carried out at each landing spot of the hopping mode during potential of zero charge (PZC) measurements. The PZC measurement protocol consists of repetitive approaches of the SECCM tip to the same location at the electrode surfaces while changing the approach potential of the sample between each consecutive approach. (b) Plots for the z position of the SECCM tip, the sample potential, and the sample current during the PZC measurement protocol at the same landing spot, which are repeats of "approach  $\rightarrow$  wait  $\rightarrow$  conditioning  $\rightarrow$  retract".

The current was measured for 2 s after each approach, followed by stepping the potential to a potential in the EDL region. This is for conditioning the electrode surface and make it free of hydrogen and oxygen adsorption before the next approach of the tip. Then, the tip was retracted, the working electrode potential was changed to the next approach potential, and the tip was approached again to the same location on electrode surface. The initial decay of the current upon contact of the SECCM tip droplet with the sample surface was fitted to the charging current equation of the series RC circuit (Equation (2-1)).

$$i = E/R_{\rm sol} \times \exp\left(-t/R_{\rm sol}C_{\rm dl}\right)$$
(2-1)

Here, *i* is the current, *t* is the time,  $R_{sol}$  is the solution resistance, and the term  $R_{sol}C_{dl}$  is the time constant ( $\tau$ ). Then, the current was integrated until the time constant calculated from the fit result, which yields the amount of the EDL charge. Finally, the PZC was evaluated by taking the x-intercept of the linear fit of EDL charge vs approach potential. The first approach data was excluded during analyses because it reflects the charging of the arbitrary surface probably having adsorption of hydrogen or oxygen.

#### 2.3.6. Hydrogen Evolution Reaction Activity Measurement

A SECCM tip with a diameter of ~3 µm was utilized to obtain HER CVs of bare Pt and the selected Pt-Pd-Ru-Ir-Ag measurement areas of the HEA-ML in 10 mM HClO4 under Ar atmosphere with a scan hopping mode of 4 X 4. The reference electrode was Ag/AgCl (3 M KCl), and the potential values were converted to the RHE scale ( $E_{RHE} = E_{substrate} + E_{Ag/AgCl} + 0.059$  pH). Here,  $E_{Ag/AgCl}$  is 0.210 V, and pH of 10 mM HClO<sub>4</sub> is 2. CV cleaning cycles within the potential window from -0.6 V to 1.4 V vs Ag/AgCl (3 M KCl) were recorded at each measurement area before the HER activity measurements. Since the same SECCM tip was utilized for all the HER experiments, the surface area was calculated from the SECCM tip area.

#### 2.3.7. Finite Element Simulations of the HER Voltammogram



**Figure 2-3.** (a) The 2D axisymmetric geometry of the model consists of the pipette body and the protruding droplet. The length of the bulk reservoir, the height of the geometry, and the radius of the wetted electrode area are 60  $\mu$ m, 500.1  $\mu$ m, and 1  $\mu$ m, respectively. (b) The mesh structure of the model. The pipette body was constituted of free triangular with extra fine element size, and the droplet was constituted of the mapped quadrangular with the minimum element size of ~1 nm. (c-d) Outline of the applied physics in the model.

Name	Value	Reference
Diffusion coefficient of H <sup>+</sup>	$9.31 \times 10^{-9} \mathrm{m^{2}/s}$	[56]
Diffusion coefficient of ClO <sub>4</sub> <sup>-</sup>	$1.79 \times 10^{-9} \text{ m}^{2/s}$	[57]
Bulk concentration of HClO <sub>4</sub>	10 mM	
pH of the electrolyte	2	
Relative dielectric constant of water at IHP	2	[26]
Relative bulk dielectric constant of water	78	[58]
Charge transfer coefficient of the Butler-Volmer kinetics	0.5	
Temperature	298 K	

 Table 2-1. The parameter values used in the numerical simulation.

The mechanism of the PZC-dependent HER voltammograms at the SECCM was investigated by the finite element simulation using COMSOL Multiphysics 5.6 software. The HER voltammogram was solved with a time-dependent study. The stationary studies were preceded to obtain the initial conditions for the timedependent studies. The geometry of the SECCM tip and the protruding droplet touching the electrode surface was modeled in 2D axisymmetric structure as depicted in Figure S14a. There was the IHP with a thickness of 0.4 nm right next to the electrode surface, where no ion transport was assumed.<sup>[23]</sup> The height of the simulated electrolyte was ca. 500 µm, which is much longer than the diffusion layer thickness ( $\sqrt{Dt} \approx 273$  µm). The simulated voltammetry at the geometry with elongated tip height did not show notable changes. Meshes are constituted of narrow mapped quadrangular discretization at the droplet and free triangular discretization at the pipette body. The smallest mesh size near the IHP of the EDL is less than 1 nm. The mesh size gradually increased as it was close to the bulk reservoir.

The transport of  $H^+$  and  $ClO_4^-$  in the electrolyte was solved using the

Nernst-Planck-Poisson equations. In this physics, the Poisson equation (Equation (2-2)) calculates the electric potential of the solution phase while the Nernst-Planck equation (Equation (2-3)) describes the diffusional and migrational flux of chemical species in the solution.

#### (1) Electrostatics: Poisson equation

$$\nabla^2 \Phi = -\frac{\sum z_i \, C_i F}{\varepsilon \varepsilon_0} \tag{2-2}$$

Here,  $\Phi$  is the electric potential,  $z_i$  and  $C_i$  is respectively the charge the concentration of the species *i*, and  $\varepsilon$  is the relative dielectric constant.  $\varepsilon$  of the water was set to be 78, while that in the IHP was 2.<sup>[26]</sup>

The ground potential ( $\Phi = 0$ ) was applied to the bulk reservoir domain. The electric potential of the electrode surface was the difference between the electrode potential and the PZC.

#### (2) Transport of diluted species: The Nernst-Planck equation

$$\frac{\partial C_i}{\partial t} = -D_i \nabla C_i - \frac{z_i F}{RT} D_i C_i \nabla \Phi \qquad (2-3)$$

Here,  $D_i$  is the diffusion coefficient of the species *i*. The concentration of the species at the bulk reservoir domain was fixed as their bulk concentrations. H<sup>+</sup> was consumed in the electrode surface because of the HER. The HER kinetics was represented by the Butler-Volmer kinetics model (Equation (2-4)).<sup>[23]</sup> Hydrogen oxidation reaction (HOR) was not considered because the HOR current was not observed in the experiment because of the Ar atmosphere and fast diffusing out of the produced H<sub>2</sub> through the droplet-air interface.

$$i = -i_{ref} \frac{C_{H^+}}{C_{H^+, ref}} \exp\left(-\frac{\alpha F}{RT} (E_{RHE} - E_{RHE, ref})\right)$$
(2-4)

The reference state (3 mA/cm<sup>2</sup> at -0.2 V vs SHE) was set to have the similar scale to the experimental HER current density on a flat Pt electrode.<sup>[59]</sup> The inward H<sup>+</sup> flux at the outer Helmholtz plane (OHP) was i/F. The current density was calculated by dividing the current by the area of the SECCM tip end, 7.0686  $\mu$ m<sup>2</sup>. This considers the actual experimental situation where the contact area of the droplet to the electrode surface is not able to be measured.

### 2.4. Results and Discussion

#### 2.4.1. Measurement of PZC of Pt and Au Surfaces by SECCM



Figure 2-4. Simplified electrical double layer (EDL) structure when the SECCM tip touches the electrode surface at a given approach potential ( $E_{approach}$ ).

A sputtered polycrystalline Pt thin-film electrode was used as model sample for initial PZC measurements because it is one of the most studied metals with a well-defined CV allowing direct comparison with reported PZC values. Typically, a single-barrel SECCM pipette with a tip diameter of ~ 1  $\mu$ m (see Figure 2-1a) filled with 10 mM aqueous HClO<sub>4</sub> solution and a Ag/AgCl (3 M KCl) reference electrode inserted from the top (see Figure 2-1b) was used in a home-built SECCM (Figure 2-2a). The SECCM tip was approached to the polarized Pt surface at a pre-defined potential until the meniscus of the droplet protruding from the end of the pipette touched the sample surface. Formation of an EDL in the moment of the contact results in a capacitive charging current (Figure 2-4). A positive charging current flows when the potential is more negative than the PZC, whereas a negative charging current flows when the potential is more negative than the PZC. By repeating the approach on the same landing spots at different applied substrate potentials, and calculating the charge upon each approach, the PZC is determined as the potential where no charge is injected or extracted upon contact. The charge associated with



**Figure 2-5.** (a) An equivalent circuit for the moment when the electrolyte meniscus of the droplet protruding from the SECCM capillary touches the sample surface, and the expected current from the series RC circuit following Equation (1). (b) Currents upon the contact of the SECCM tip to the Pt at approach potentials from 0.2 V to 0.6 V vs Ag/AgCl (3 M KCl). (c) Linear fitting result of the EDL charge vs approach potential. The EDL charges were calculated by integration of the initial charging currents up to the time constant derived by exponential fitting (see Figure S3). The x-intercept, 0.49 V, is the PZC. (d) Time constant in dependence from the approach potentials. The minimum time constant was achieved at potentials close to PZC. (e, g) Typical surface-cleaning voltammograms at (e) Pt and (g) Au with a scan rate of 1 V/s conducted before PZC experiments. (f, h) Comparison of the PZC values at (f) Pt and (h) Au before and after the cleaning CVs.



**Figure 2-6.** Exponential fitting results of the initial current upon the contact at the approach potentials of (a) 0.6 V, (b) 0.5 V, (c) 0.4 V, (d) 0.3 V, and (e) 0.2 V vs Ag/AgCl (3 M KCl) to Equation (2-1).

the formation of the EDL ( $C_{EDL}$ ) at different applied potentials was evaluated by integration of the current trace up to  $\tau$ . The duration of  $\tau$  was chosen to avoid possible interference by faradaic currents on the total charge. Faradaic reactions cannot occur until the interface is sufficiently charged. During the experiments, there are no redoxactive species in the electrolyte and  $CIO_4^-$  is a non-adsorbing anion. Hence, the situation when the droplet touches the sample surface corresponds to that of a serial RC circuit being connected as shown in **Figure 2-5a**. This accompanies a current peak with an exponential decay that can be represented by Equation (2-1).  $\tau$  was obtained by fitting the initial current upon contact of the electrolyte to the electrode surface to Equation (1) to allow for comparison of data from different SECCM pipettes which may not form electrochemical cells of exactly the same size.

**Figure 2-5b** and **Figure 2-6** shows the currents recorded upon contact of the SECCM tip meniscus to the Pt surface at various approach potentials from 0.2 V

to 0.6 V vs Ag/AgCl (3 M KCl). If the approach potential is close to the hydrogen adsorption or Pt oxide formation region, the current was deviated from Equation (1) (see **Figure 2-6**). The corresponding  $C_{EDL}$  was plotted against the approach potential (**Figure 2-5**c) exhibiting an x-intercept of 0.49 V vs Ag/AgCl (3 M KCl), corresponding to the PZC. A plot of the corresponding time constants over the applied potential during approach of the SECCM tip to the Pt surface (**Figure 2-5**d) revealed a local minimum of  $\tau$  at around the PZC. This is expected since the  $R_{sol}$  is only dependent on the conductivity of the electrolyte and the shape of the electrochemical cell, and  $C_{dl}$  is minimal near PZC according to the Gouy-Chapmann model for the EDL structure of a diluted electrolyte.<sup>[60]</sup> Before retraction of the tip after each approach, the electrode potential was switched to the double layer region, here 0.2 V vs Ag/AgCl (3 M KCl), to release any adsorbed oxygen or hydrogen, so that upon the next approach, the EDL would be formed on the pre-conditioned electrode surface.<sup>[53]</sup>

This PZC measurement protocol  $[n^*(approach-wait-condition-retract)]$  is deployed at multiple landing spots on the Pt surface using a regular rectangular grid hopping mode (9 x 9 independent measurements) to provide statistical reliability. In order to ensure similar surface conditions for each spot, 5 CV cycles were performed after the first approach at a landing site for surface cleaning purposes before the PZC protocol is executed. The full protocol on each spot is therefore: approach, surfacecleaning CV, retract, and PZC measurement, as depicted schematically in **Figure 2-2**. The reference electrode potential was calibrated before and after each SECCM measurement, and all electrochemical experiments were conducted under Ar atmosphere to avoid any interference caused by O<sub>2</sub> as shown in **Figure 2-7**.



**Figure 2-7.** Cyclic voltammograms (CV) in 10 mM HClO<sub>4</sub> at IrHEA (#8 of the Pt-Pd-Ir-Ru-Ag HEA) with Ar flow (blue) and without Ar flow (orange).

Figure 2-5f compares the PZC histogram for polycrystalline Pt measured before and after the surface-cleaning CV (Figure 2-5e) at 9 x 9 landing spots with a hopping distance of 10  $\mu$ m. Data with  $R^2$  less than 0.9 in the linear fit of  $C_{EDL}$  vs approach potential were not considered. The PZC of the Pt without cleaning was  $0.34 \pm 0.02$  V vs Ag/AgCl (3 M KCl) (N = 74) while the PZC of Pt after cleaning was  $0.44 \pm 0.02$  V vs Ag/AgCl (3 M KCl) (N = 57). The PZC after surface-cleaning is about 100 mV higher, and unsurprisingly more consistent with the previously reported PZC value for Pt using SECCM (0.7 V vs SHE = 0.49 V vs Ag/AgCl/3 M KCl),<sup>[53]</sup> and in line with the value measured by the immersion technique.<sup>[61]</sup> Performing voltammetry can significantly decrease contamination at electrode surfaces.<sup>[62]</sup> A sputtered polycrystalline Au thin-film electrode was used as a second sample for validation of the protocol. The PZC of Au was  $0.29 \pm 0.02$  V (N = 46) before the cleaning process, and  $0.26 \pm 0.03$  V (N = 62) after the cleaning process (Figure 2-5g-h). The PZC after cleaning agrees well with the previously reported PZC of Au.<sup>[61,63]</sup> It is worth noting that the PZC values of Pt and Au considerably depend on their crystalline facets.<sup>[53]</sup> For example, the potential of maximum entropy (PME) of Pt(111) which is nearly equivalent to the PZC is about 250 mV higher than that of Pt(110).<sup>[64]</sup> PZC values determined by the minimum  $C_{dl}$  method displayed a maximum difference of about 0.4 V in dependence of the exposed Au surface structure.<sup>[65]</sup>

# 2.4.2. PZC Values of a Pt-Pd-Ru-Ir-Ag HEA-ML Evaluated by Means of SECCM

A thin-film noble-metal HEA-ML with Pt-Pd-Ru-Ir-Ag as constituting elements was used to study the composition effect on the PZC. The Pt-Pd-Ru-Ir-Ag ML was prepared by a single combinatorial co-sputtering process of all elements on a sapphire wafer.<sup>[32]</sup> Simultaneous sputtering of multiple elements has successfully fabricated thin-film type HEA consisting of noble metals<sup>[32,49]</sup> or non-noble metals<sup>[66]</sup> and even high-entropy oxides<sup>[67]</sup> with a continuous compositional gradient of each element. Their atomic level mixing has been characterized by EDX and atom probe tomography (APT).<sup>[32,49]</sup> Here, the noble metal HEA was selected because noble metals possess high electrochemical stability and allow for multiple cleaning CVs with negligible dissolution of the individual constituent elements. The elemental composition (atomic %) of each measurement area (MA) on the HEA-ML was measured by EDX, and the results are shown in **Figure 2-8**. Elemental compositions of MAs for which electrochemical experiments were performed on the HEA-ML can be found in **Table 2-2**. The X-ray diffraction (XRD) pattern of the HEA-ML (**Figure 2-10**) confirms single-crystalline phase fcc lattice structure.



**Figure 2-8.** Color-coded visualization of the composition gradients and composition ranges of the Pt-Pd-Ru-Ir-Ag high-entropy alloy material library (HEA-ML) measured by energy dispersive X-ray (EDX) analysis in atomic percentage (atomic %).



**Figure 2-9.** Pie chart diagram indicating the relative elemental compositions at each of measurement area (MA) of the Pt-Pd-Ru-Ir-Ag HEA-ML.

MA name	Pt %	Pd %	Ir %	Ru %	Ag %	Estimated WF (eV)
#1	31.2	43.3	9.8	14.2	1.4	5.24
#2 (PtHEA)	32.3	45.2	9.0	12.5	9.7	5.25
#3	26.5	44.6	11.7	16.1	1.1	5.21
#4 (RuHEA)	18	38.4	18.0	24.3	1.3	5.14
#5	19.6	45.6	16.1	17.6	1.1	5.17
#6 (PdHEA)	17.8	62.1	11.3	8.0	0.8	5.19
#7	13.4	33.6	23.8	27.9	1.4	5.11
#8 (IrHEA)	12.2	39.9	26.2	21.0	0.9	5.13

**Table 2-2.** Atomic % of each element and the estimated work function (WF) at eight locations in Pt-Pd-Ir-Ru-Ag HEA-ML where SECCM experiments were carried out.



**Figure 2-10.** X-ray diffraction (XRD) patterns of the eight MAs (MA #1 - #8) and the reference XRD peaks of the PdPt fcc lattice.<sup>[68]</sup>

To investigate the overall effects of elemental composition (Ag is not considered due to its low content across the HEA-ML) of the HEA-ML on the PZC values, four MAs on the HEA-ML with the highest content of one of the constituent elements were selected for SECCM PZC measurements, namely: PtHEA (MA #2), PdHEA (MA #6), IrHEA (MA #8), and RuHEA (MA #4). Here, the PZC was also measured after cleaning CVs (Figure 2-11) and the conditioning potential was chosen to be 0.1 V, a value within the double layer region regardless of the elemental composition of the HEA. Interestingly, the PZC values of PtHEA, PdHEA, IrHEA, and RuHEA follow the work function trend of these elements (Figure 2-12a and Table 2-3). The work function values of Pt, Pd, Ir, Ru, and Ag are 5.7 eV, 5.1 eV, 5.3 eV, 4.7 eV, and 4.3 eV, respectively.<sup>[69]</sup> The slightly higher PZC value of PdHEA than that of IrHEA may be due to its 5.6% higher content of Pt having the highest WF among all constituting elements. The PZC values of PtHEA, PdHEA, IrHEA, and RuHEA measured without surface-cleaning CVs exhibit a different PZC trend (Figure 2-12b), and the trend was less clear and had bigger standard deviations. This corroborates the significance of the surface-cleaning procedure right before the PZC measurements.

	Without surface	Without surface-cleaning CV		After surface-cleaning CV	
	PZC	The number of data	PZC	The number of data	
RuHEA	$0.29\pm0.02~V$	88	$0.23\pm0.01~V$	38	
IrHEA	$0.29\pm0.02~V$	84	$0.24\pm0.02~V$	59	
PdHEA	$0.30\pm0.02~V$	64	$0.30\pm0.01~V$	83	
PtHEA	$0.33\pm0.09\;V$	96	$0.39\pm0.03~V$	86	

**Table 2-3.** Summary of the PZC distributions of in RuHEA, IrHEA, PdHEA, and PtHEA before and after surface-cleaning CV.



**Figure 2-11.** Typical surface-cleaning CVs of (a) RuHEA, (b) IrHEA, (c) PdHEA, and (d) PtHEA with a scan rate of 1 V/s in 10 mM HClO<sub>4</sub> under Ar atmosphere.



**Figure 2-12.** (a) Primary element effects on PZC of the Pt-Pd-Ru-Ir-Ag. PZC of four locations are investigated after surface-cleaning CV at RuHEA, IrHEA, PdHEA and PtHEA in 10 mM HClO<sub>4</sub>. (b) The PZC of the HEA-ML, which did not undergo surface-cleaning, showed little difference according to element content.



**Figure 2-13.** Color-coded visualization of the estimated WF values of the Pt-Pd-Ru-Ir-Ag HEA-ML. The selected eight MAs for PZC investigation with SECCM are marked with black line-squares. Elemental compositions of all eight MAs are listed in **Table 2-2**.

Inspired by this result, we introduced the estimated WF as a parameter to quantitatively explain the relationship between the PZC and the composition of the HEA. The estimated WF is the composition-weighted average of the WF values of the individual constituent elements as represented in Equation (2-5):

Estimated WF = 
$$\sum x_k WF_k$$
 (2-5)

Here,  $x_k$  is the atomic fraction of each element measured by EDX, and WF<sub>k</sub> is its WF. **Figure 2-13** shows a surface map of the estimated WF and the black square marked regions show the location of eight MAs selected to cover the estimated WF range of the Pt-Pd-Ru-Ir-Ag HEA-ML from 5.11 eV to 5.25 eV. The PZC values at these locations were evaluated with the same PZC protocol after cleaning CVs (**Figure 2-14**), and the results are shown in **Table 2-4**.

	PZC	The number of data
#1	$0.35\pm0.04\;\mathrm{V}$	79
#3	$0.32\pm0.02\;\mathrm{V}$	66
#5	$0.28\pm0.02\;\mathrm{V}$	73
#7	$0.23\pm0.02\;V$	62

**Table 2-4.** Summary of the PZC distributions of the four locations of Pt-Pd-Ru-Ir-Ag, (a) #1, (b) #3, (c) #5, and (d) #7, after surface-cleaning CV.



**Figure 2-14.** Typical surface-cleaning CVs of the four locations of Pt-Pd-Ru-Ir-Ag, (a) #1, (b) #3, (c) #5, and (d) #7, with a scan rate of 1 V/s in 10 mM HClO<sub>4</sub> under Ar atmosphere.



**Figure 2-15.** The linear correlation of the PZC values of the selected eight MAs to the estimated WF values exhibits a slope of 1

**Figure 2-15** shows the relationship between PZC and the estimated WF at eight MAs of the Pt-Pd-Ru-Ir-Ag HEA-ML. Interestingly, the PZC values of the Pt-Pd-Ru-Ir-Ag compositions show a positive correlation with the estimated WF and the line of best fit exhibits a slope of unity. Even though RuHEA and IrHEA have different elemental compositions, similar PZC values were measured, with an average of 0.23–0.24 V, which can be explained by their similar estimated WF of 5.13–5.14 eV. A linear relationship between PZC and WF of electrodes has been theoretically suggested:<sup>[1,70]</sup>

$$PZC = WF + \delta x^{M} - g_{dipole}^{S} + K$$
(2-6)

where  $\delta x^{M}$  is the change in the surface potential of an electrode upon contact with water,  $g_{dipole}^{S}$  is the surface potential of the solution side that has a contact with the electrode, and *K* is the potential drop at the reference electrode/solution interface. Equation (2-6) was corroborated for pure metals, e.g. Trasatti showed two distinct relationships for sp-metals (PZC = WF – 4.69), and for transition metals (PZC = WF – 5.01).<sup>[1]</sup> The x-intercept of the PZC dependence on the estimated WF of the Pt-Pd-Ru-Ir-Ag HEA-ML is with 4.9 eV similar to literature values, which validates our

finding of a slope of unity for PZC vs estimated WF. The difference of the x-intercept values with respect to the literature values can be attributed to the EDL structure, because the x-intercept includes the terms of both the electrode's and the electrolyte's surface potentials as shown in Equation (2-6), and the WF itself contains the surface potential of the electrode. Computational studies reveal that the direction in which the first-layer water molecules face the electrode affects PZC,<sup>[71,72]</sup> and adsorption of halides significantly alters WF.<sup>[73]</sup> Some studies have suggested a pH dependence<sup>[74,75]</sup> and a cation dependence of the PME.<sup>[76]</sup>

# 2.4.3. Correlation of PZC and HER Electrocatalytic Activities Determined from a Pt-Pd-Ru-Ir-Ag HEA-ML

The measured PZC values of the Pt-Pd-Ir-Ru-Ag HEA-ML— which range from 0.2 V to 0.4 V vs Ag/AgCl—are wide enough to identify a possible correlation of the PZC values with electrocatalytic properties. We investigated the HER at selected regions of the Pt-Pd-Ir-Ru-Ag HEA-ML. The HER activity was determined by acquiring CVs at a scan rate of 0.1 V/s using a 4 x 4 scan-hopping procedure (16 independent landing spots) at the eight MAs of the Pt-Pd-Ru-Ir-Ag HEA-ML as well as on polycrystalline Pt (**Figure 2-16**). A SECCM tip with a diameter of ~3  $\mu$ m filled with 10 mM HClO<sub>4</sub> was used for all HER suggesting that the droplet area at the end of the SECCM tip did not change significantly during the scan-hopping experiments. For Pt, the HER current increases from around 0 V vs RHE while the HEA surfaces show an initial cathodic process before the HER, which is likely due to hydrogen adsorption and desorption on the Pd surface atoms.<sup>[77]</sup>



**Figure 2-16.** HER CVs in 10 mM HClO<sub>4</sub> under Ar atmosphere at (a) Pt and (b–i) the eight MAs of the Pt-Pd-Ru-Ir-Ag with a scan rate of 0.1 V/s measured by SECCM. The straight lines show the average responses, and the green-coloured patches represent their standard deviations from 16 independent scan-hopping experiments. Arrows in (a) represent the direction of the scan.



**Figure 2-17.** The relationship between HER current density and PZC at bare Pt and the Pt-Pd-Ru-Ir-Ag depending on the overpotential of (a) -50 mV, (b) -150 mV, and (c) -200 mV vs RHE. HER current values are taken from the forward scan of **Figure 2-16**. Error bars represent the standard deviations of the averaging.



**Figure 2-18.** The relationship between the HER current density and PZC at bare Pt and the Pt-Pd-Ru-Ir-Ag depending on the overpotential of (a) -50 mV, (b) -100 mV, (c) -150 mV, and (d) -200 mV vs RHE. HER current values are taken from the backward scan of **Figure 2-16**. Error bars represent the standard deviations of the averaging.



**Figure 2-19.** The relationship between HER current density at -100 mV vs RHE, the peak potential ( $E_{\text{peak}}$ ) of the CV, and PZC investigated at Pt and the eight MAs of the Pt-Pd-Ru-Ir-Ag HEA catalyst. HER current density values and  $E_{\text{peak}}$ , the potential value with the largest current density in the CV, are obtained from the forward scan of **Figure 2-16**. Error bars represent the standard deviations.

**Figure 2-19** summarizes the relationship between HER activity and PZC at Pt and the eight MAs of the Pt-Pd-Ru-Ir-Ag HEA-ML. There is a positive correlation between the HER current density and the PZC until the potential reaches the masstransport limited region (-0.2 V vs RHE) (see **Figure 2-17**). The correlation was also slightly perturbed at lower overpotentials (-50 mV vs RHE) because of the influence from an initial cathodic reaction at the HEA surfaces which is even occurring at potentials > 0 V vs RHE. It should be noted that the SECCM experiments measuring HER were carried out in random order irrespective of the order of PZC. This positive correlation was observed as well in the backward scan of the CVs where the initial cathodic reaction is not present (see **Figure 2-18**). Moreover, the CVs exhibited slight peaks in their forward scan. Figure 5d shows the positive shift of peak potentials ( $E_{peak}$ ) with more positive PZC where the trend followed that of the current density vs PZC.

Higher HER activity was recorded for HEA compositions with higher PZC values. This correlation is contrary to that of alkaline HER electrocatalysis. The sluggish alkaline HER kinetics at electrodes exhibiting higher PZC has been attributed to the electric field-induced disadvantage in the reorganization of the water network, <sup>[17,18,78]</sup> and the poor hydrogen bonding network in the EDL.<sup>[19]</sup> Nevertheless, revisiting the previously revealed positive correlation between PZC and the WF, the observation is in line with the report of Trasatti showing that metals with higher WF had enhanced activity for the HER in acidic electrolytes as measured in terms of exchange current.<sup>[1]</sup>

# 2.4.4. Finite Element Simulation to Elucidate the Surface Charge Effects on the Acidic HER

Numerical modeling of the HER in the SECCM system by COMSOL Multiphysics version 5.6 was employed to understand the electrode surface charge effects on the HER voltammograms. The 2D axisymmetric geometry of the SECCM tip and the droplet at the end of the tip was discretized with fine triangular and quadrangular meshes (**Figure 2-3a, b**). The Nernst-Planck-Poisson equation was employed to demonstrate the transport of H<sup>+</sup> and  $ClO_4^-$  in the SECCM electrochemical cell in response to the electric potential distribution in the EDL, and the HER kinetics in the model followed the Butler-Volmer kinetics (**Figure 2-3c, d**).



**Figure 2-20.** (a) Simulated HER CVs on a range of the electrode PZC values from 0.2 V to 0.45 V. (b) The relationship between HER current density,  $E_{\text{peak}}$ , and the electrode PZC predicted by the finite element simulation.

A time dependent study yielded the sigmoidal HER voltammograms with slight peak shape (**Figure 2-20a**), which were observed in the experimental HER voltammograms (**Figure 2-16**). The simulated HER CV shifted to the cathodic potential with more negative electrode PZC. As shown in **Figure 2-20**, the current density became higher with more positive electrode PZC until the potential reached ca.  $-170 \text{ mV} \sim -200 \text{ mV}$  vs RHE. It became independent of PZC at more negative potentials, meaning that the current was fully governed by mass transport. These two features were displayed in the experimental data (**Figure 2-17** and **Figure 2-18**). The PZC-dependent  $E_{\text{peak}}$  was also reproduced in the simulation as shown in **Figure 2-20b**. The peaks in the forward scan of the HER CVs can be understood by the transient of the diffusional flux shape across the electrode potential.

Figure 2-21 demonstrates the concentration profile of H<sup>+</sup> and ClO<sub>4</sub><sup>-</sup> while HER occurs. For instance, the CV at the PZC of 0.45 V displayed the  $E_{\text{peak}}$  at -0.172 V, and the local concentration of  $H^+(C_{H^+})$  dropped to zero at -0.172 V (see Figure **2-21b** –d). Otherwise, in the case of the PZC value of 0.25 V, the local  $C_{H^+}$  was not zero at -0.172 V, and it fell to zero after the potential exceeded its  $E_{\text{peak}}$  (see Figure 2-21h-j). Once  $C_{H^+}$  at the interface drops to zero, the diffusion layer widens with time. The decrease in the concentration gradient for the reactant results in the reduced current, causing a peak in the CV. Then, when the electrode potential  $> E_{\text{peak}}$ , the current became fully governed by the mass transport flux of H<sup>+</sup> along the SECCM pipette body as shown in Figure 2-22, and lost the PZC-dependent current behaviors. On the other hand, the simulation without considering the potential distribution in the electrode-electrolyte interface and the migration of H<sup>+</sup> and ClO<sub>4</sub><sup>-</sup> generated the CV (Figure 2-23) with no peak and smaller current density compared to Figure 2-20a. This indicates that the ion distribution in the EDL is the significant factor determining the sigmoidal voltammogram with small peaks and its PZC dependent responses.



**Figure 2-21.** (a) Simulated HER voltammogram at the electrode PZC of 0.25 V and 0.45 V. To understand the peak shaped sigmoidal voltammogram, the concentration profiles of H<sup>+</sup> and ClO<sub>4</sub><sup>-</sup> are investigated at the forward scan of the potential (*E*): -0.15 V, -0.172 V (peak potential of the CV on the electrode PZC 0.45 V), and -0.2 V. These points are designated as black dots in (a). (b-g) H<sup>+</sup> and ClO<sub>4</sub><sup>-</sup> concentration profile and the magnified H<sup>+</sup> concentration profile at the electrode PZC of 0.45 V (b, e) at -0.15 V, (c, f) at -0.172 V, and (d, g) at -0.2 V. At  $E = E_{peak}$ , -0.172 V, H<sup>+</sup> begins to deplete at the electrode surface. (h-m) H<sup>+</sup> and ClO<sub>4</sub><sup>-</sup> concentration profile and the magnified H<sup>+</sup> concentration profile at the electrode with a PZC of 0.25 V (h, k) at -0.15 V, (i, 1) at -0.172 V, and (j, m) at -0.2 V. Unlike the case of the PZC 0.45 V, the local concentration of H<sup>+</sup> did not reach zero at -0.172 V. It becomes depleted at the electrode surface when  $E < E_{peak}$ . The sharp increase in H<sup>+</sup> concentration and decrease in ClO<sub>4</sub><sup>-</sup> concentration in the vicinity of the electrode surface are to compensate for the negative surface charge of the electrode.



**Figure 2-22.** The potential (*E*) dependent profile of the H<sup>+</sup> concentration and H<sup>+</sup> flux near the electrode surface up to about 6.5 µm height along the pipette when the electrode PZC is (a-c) 0.45 V and (d-f) 0.25V. The size of the arrowhead is proportional to the flux magnitude. (a), (d), and (e) are before *E* reaches their  $E_{\text{peak}}$ , and (b), (c), and (f) are after *E* reaches their  $E_{\text{peak}}$ . ( $E_{\text{peak}}$  of the PZC 0.45 V case and the PZC of 0.25 V case are -0.172 V and -0.195 V, respectively.) (a), (d), and (e) feature the incomplete depletion of H<sup>+</sup> on the electrode surface and the spherical flux of H<sup>+</sup> near the electrode. In (b), (c), and (f), H<sup>+</sup> is fully consumed at the droplet, and the transport of H<sup>+</sup> along the pipette body determines the supply of H<sup>+</sup> to the electrode surface.



**Figure 2-23.** Simulated HER voltammogram without considering migrational flux of species in the electrolyte.



**Figure 2-24.** (a-b) Electric potential and electric field profile near the electrode surface at -0.1 V vs RHE with the electrode PZC of 0.25 V and 0.45 V. (c) H<sup>+</sup> concentration at the outer Helmholtz plane (OHP) across the electrode PZC at -0.1 V vs RHE.

Figure 2-24a, b compares the electric potential and the electric field distribution of the EDL at -100 mV vs RHE across the electrode PZC. The more positive the electrode PZC is, the stronger the electric field is applied to the interface and the thicker EDL becomes while HER occurs. This is because the potentials for HER are more negative than that of the PZC. Therefore, cations rather than anions mainly occupy the EDL to compensate for the negative surface charge of the electrode, and the only cation in 10 mM HClO<sub>4</sub> is H<sup>+</sup> which is the reactant for HER. Thus, the concentration of the H<sup>+</sup> is supposed to increase on the surface of the electrode where PZC is more positive. Indeed, from 16- to 28-fold preconcentration of H<sup>+</sup> was observed in the simulation (Figure 2-24c). The average concentration of H<sup>+</sup> at the outer Helmholtz plane in the simulation increased with the electrode PZC values with the same slope as the current density vs PZC slope in Figure 2-20b (1.67 times increase at the PZC value of 0.45 V compared to that of 0.2 V). This leads us to the conclusion that the preconcentration of H<sup>+</sup> should be more pronounced when the PZC is more positive and could explain the correlation between PZC, WF and HER activity. On the contrary, this preconcentration effect should be diminished in the alkaline HER, where the reactant for the HER is H<sub>2</sub>O with neutral charge. This may

be the reason for the contradicting role of the electrode PZC on the HER activities in acidic and alkaline conditions.

HEA electrocatalysts have gained considerable interest as a HER electrocatalyst for their ability to reach good catalytic performance through fine tuning the electronic structure and their outstanding stability caused by their high mixing entropy.<sup>[28,79]</sup> The HER catalytic activities of HEA according to its elemental composition have solely been explained by the hydrogen binding energy of HEA, which necessitates DFT computation.<sup>[79,80]</sup> Despite the corroborated usefulness of the Sabatier principle as a HEA designing principle for HER electrocatalyst, it mainly predicts the thermodynamics of the reaction pathway, and could oversimplify the role of reaction environment surrounding reactants, such as electric field, solvation structure, and ionic distribution in the EDL.<sup>[8]</sup> In spite of the possibility that the elemental composition of HEA can modify the hydrogen binding energy, what we found in this study suggests that the electrode PZC according to the elemental composition of the HEA and correspondingly altered EDL structure can significantly contribute to the acidic HER electrocatalysis at the HEA. Finite element simulation attributes the PZC effect to the preconcentration of H<sup>+</sup>, the reactant for the HER, in the EDL.

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### 2.5. Conclusion

In summary, we explored the PZC of HEA compositions and its effects on the acidic HER for the first time through the high-throughput analysis using SECCM and the Pt-Pd-Ru-Ir-Ag HEA-ML. For the local PZCs at the Pt-Pd-Ru-Ir-Ag HEA-ML with known elemental composition, we propose that the PZC can be determined from the estimated WF according to the relationship, PZC = estimated WF – 4.9. The wide PZC range of a single Pt-Pd-Ru-Ir-Ag HEA-ML enables the possibility to experimentally elicit the positive correlation of PZC and HER current density without the effect of sample preparation history. Numerical modeling of the EDL structure during HER supports that a negative interfacial electric field at HEA compositions having a higher PZC value gives rise to preconcentration of H<sup>+</sup> in the EDL. The numerous elemental combinations and ratios of surfaces of the HEA-ML could provide highly active sites for electrochemical reactions, which in turn makes it complex to predict HEA properties. Our work contributes to this, suggesting a tool for the prediction of the PZC of compositional-different areas of a HEA-ML.

## 2.6. Acknowledgements

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# Chapter 3. Heterogeneous Electron Transfer Reorganization Energy at the Inner Helmholtz Plane in a Polybromide Ionic Liquid

In this study, we present a methodology to assess the reorganization energy associated with the reduction of  $Br_2$  in a polybromide ionic liquid. The reorganization energy encompasses valuable information regarding the solvation structure within the inner Helmholtz plane, where the electron transfer takes place. Consequently, this methodology facilitates the exploration of the surface charge-sensitive electrical double layer structure in ionic liquids.

The work discussed in this chapter has been published. Sangmee Park and I were responsible for conducting the experiments, analyzing data, and preparing the paper. The initial experimentation results appear in her thesis, which has been reanalyzed and improved in this chapter. This work was supervised by Taek Dong Chung.

# Heterogeneous Electron Transfer Reorganization Energy at the Inner Helmholtz Plane in a Polybromide Ionic Liquid

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## 3.1. Abstract

In ionic liquids (ILs), the EDL is where heterogeneous electron transfer (ET) occurs. Nevertheless, the relationship between the EDL structure and its kinetics has been rarely studied, especially for ET taking place in IHP. This is largely because of the lack of an appropriate model system for experiments. In this work, we determined the reorganization energy of  $Br_2$  reduction in a redox-active IL, 1-ethyl-1-methylpyrrolidinium polybromide (MEPBr<sub>2n+1</sub>) based on the Marcus-Hush-Chidsey model. Exceptionally fast mass transport of  $Br_2$  in MEPBr<sub>2n+1</sub> allows to obtain voltammograms in which the current plateau is regulated by electron-transfer kinetics. This enables investigation of the microscopic environment in the IHP of the IL affecting electrocatalytic reactions through reorganization energy. As a demonstration, TiO<sub>2</sub>-modified Pt was employed to show pH-dependent reorganization energy, which suggests the switch of major ions at the IHP as a function of surface charges of electrodes.

**Keywords** : Ionic liquids (ILs) • Electrical Double Layer (EDL) structure • Marcus-Hush-Chidsey model • Reorganization energy • Surface Charge

# **3.2.** Introduction

The EDL structure is critical to understand and predict the activities of electrochemical reactions.<sup>[15,17,18]</sup> For example, the enhanced HER/HOR activities using a Ni(OH)<sub>2</sub>-modified Pt (111) electrode were ascribed to the shift in the PZC of Pt via structural changes in the EDL.<sup>[17,18]</sup> Applying a strong electric field  $(10^8-10^{10} \text{ V/m})$  gives rise to the rearrangement and reorientation of electrolytes in vicinity to the electrode surface, creating a unique medium for heterogeneous electron transfer. The dielectric constant of solvents closer to the electrode is smaller than that of bulk,<sup>[81-83]</sup> making reorganization energy decrease.<sup>[26]</sup> This phenomenon highlights in the IHP where the electric field is the strongest across the EDLs.

The impact of interfacial electric field on electrochemical activities is more prominent in RT-ILs. RT-ILs have attracted considerable interest in the field of electrocatalysis,<sup>[84,85]</sup> batteries<sup>[86]</sup> and supercapacitors<sup>[87]</sup> because of their high ionic conductivity, wide electrochemical window, and high thermal stability.<sup>[88]</sup> The extremely high ionic strength of RT-ILs leads to a unique EDL structure that is different from those of conventional electrolytes in solution. The EDL of a RT-IL is compact and consists of densely packed ions.<sup>[89]</sup> An ion in the EDL of a RT-IL strongly interacts surrounding ions and ionic composition at the surface is likely to respond to the electrode charge.<sup>[90]</sup> That is where heterogeneous electron transfer takes place so that quantitative analysis should be essential to understand the origins of many phenomena in RT-IL, including PZC-sensitive electrochemical reactions. Nevertheless, few studies have addressed the relationship between the EDL structure and electrochemical activities in RT-ILs.<sup>[91,92]</sup> This is primarily because it is hard to probe the properties of the RT-IL near the electrode, especially in the IHP.

The MHC model for heterogeneous electron transfer kinetics has been successfully applied to associate electron transfer kinetics with the microscopic properties of electrode–electrolyte interfaces.<sup>[14,15,24,26,93,94]</sup> According to the Marcus theory, the  $\lambda$  reflects the properties of medium and can be utilized to evaluate the local  $\varepsilon$  value in an EDL.<sup>[83]</sup>  $\lambda$  can be calculated by fitting the electron transfer rate vs electrode potential curve to the corresponding equation based on MHC model. Yet experimental quantitation of  $\lambda$  for electrochemical systems is challenging. Because mass transport (MT) is slower than ET in most electrochemical systems, one can hardly assume that given voltammogram reflect the ET kinetics predominantly. Most of the previous studies to measure  $\lambda$  were performed for redox species immobilized on electrode where the number of redox-active species were fixed.<sup>[93,94]</sup> Once the molecules are anchored on the electrode, EDL structure should get perturbed. Moreover, only  $\lambda$  of the OHP could be obtained for the redox species that reside at a large distance from the electrode beyond the IHP. Considering that majority of the important catalytic reactions take place in IHP accompanying adsorptive processes, it is crucial to evaluate  $\lambda$  of the IHP and look into the microenvironment in there. That requires a proper model system that allows experimental measurements varying with reaction conditions. It is more significant in RT-ILs because the high viscosity slows down the diffusion of the redox-active species, resulting in obscure interpretation of the kinetics based on currents.<sup>[95,96]</sup>

In this study, we suggest a  $Br_2$  reduction in of MEPBr<sub>2n+1</sub>, which is a  $Br^{-}/Br_{2n+1}^{-}$ -based RT-IL, as an appropriate system to investigate the effects of ion environment and PZC involved in heterogeneous ET kinetics. The mass transport of  $Br^{-}/Br_2$  in MEPBr<sub>2n+1</sub> is even faster than proton hopping,<sup>[97]</sup> and this substantially expands ET kinetics-governed potential window. In the MEPBr<sub>2n+1</sub> system, the

voltammograms are well fitted to the MHC model for heterogeneous ET kinetics, including clear ET-limited steady-state current. As a demonstration, the  $\lambda$  values of Pt and TiO<sub>2</sub>-modified Pt electrodes were compared to determine the influence of electrode surface charges.

# **3.3.** Experimental Methods

#### 3.3.1. Materials

1-ethyl-1-methylpyrrolidinium bromide (MEPBr, >99 %), 1-butyl-1methylpyrrolidinium bromide (MBPBr, >99 %), potassium phosphate monobasic (KH<sub>2</sub>PO<sub>4</sub>,  $\geq$ 99.0%), potassium phosphate dibasic (K<sub>2</sub>HPO<sub>4</sub>,  $\geq$ 98%), titanium(III) chloride solution (TiCl<sub>3</sub>, 12% Ti in HCl solution) and sodium bicarbonate (NaHCO<sub>3</sub>, 99.7-100.3%) was purchased from Sigma-Aldrich. Phosphoric acid (H<sub>3</sub>PO<sub>4</sub>, 85%) was purchased from Acros Organics. All chemicals were used as received. All solutions were prepared with Milli-Q deionized water.

#### 3.3.2. Synthesis of Polybromide Ionic Liquids

1-ethyl-1-methylpyrrolidinium polybromide (MEPBr<sub>2n+1</sub>) was electrochemically synthesized in a three-electrode system in 250 mM MEPBr aqueous, 1 M potassium phosphate buffer solution as previously reported.<sup>[97]</sup> A Compactstat potentiostat (Ivium Technologies) and PGSTAT302N (Metrohm AG) were used for electrochemical measurements. Ag/AgBr (3 M KBr) and Pt wire were used as a reference electrode and a counter electrode, respectively. Pt macroelectrode was used as the working electrode, and the diameter of Pt exposed to the solution was longer than 3 mm. 1.2 V vs Ag/AgBr was applied overnight to synthesize MEPBr<sub>2n+1</sub> droplet. The droplet was dark orangish-brown and several mm in size. 1-butyl-1methylpyrrolidinium polybromide (MBPBr<sub>2n+1</sub>) was synthesized using the same method.



**Figure 3-1. Experimental Scheme.** (a) Illustration of electrochemical measurements set-up where an UME is dipped in the MEPBr<sub>2n+1</sub> droplet that was electrochemically synthesized at (4) Pt macroelectrode in 250 mM MEPBr, 1 M potassium phosphate buffer aqueous solution. (b) CVs in MEPBr<sub>2n+1</sub> with pH 3 phosphate buffer at Pt ultramicroelectrode (UME) (diameter 50  $\mu$ m). Scan rate is 10 mV/s. The red line is measured when a reference electrode was (1) Ag/AgBr (3 M KBr), and a counter electrode was (2) Pt wire. Both electrodes were located in the aqueous solution as depicted in Fig. S1a. The blue line is measured when (4) Pt macroelectrode was utilized as both a reference electrode and a counter electrode. This result indicates that the interfacial impedance between MEPBr<sub>2n+1</sub> and the aqueous solution is negligible.

A Compactstat potentiostat (Ivium Technologies), PGSTAT302N (Metrohm AG) or CHI 660E (CH Instruments) was used for electrochemical measurements. A Pt or carbon ultramicroelectrode (UME) dipped into the synthesized MEPBr<sub>2n+1</sub> droplet was used as a working electrode. All UMEs were purchased from commercial vendors (CH Instruments, BASi and Metrohm AG). The contact between the UME and MEPBr<sub>2n+1</sub> was confirmed via the change of the open circuit potential. UMEs were mechanically polished with the silicon carbide grinding paper (CarbiMet) before the electrochemical measurements. The reference electrode is either Ag/AgBr (3M KBr) or the Pt macroelectrode used as working electrode during MEPBr<sub>2n+1</sub> synthesis. **Figure 3-1a** illustrates the electrochemical set-up. Since the area of the MEPBr<sub>2n+1</sub>/aqueous solution interface was 3-5 orders larger than the size of the UME, impedance at the interface was negligible<sup>[97]</sup> (see Figure 3-1b).

#### **3.3.4.** Preparation of TiO<sub>2</sub> Deposited Pt UME

TiO<sub>2</sub>-modified Pt electrodes (TiO<sub>2</sub>@Pt) were prepared using a method described in the previous report.<sup>[98]</sup> To briefly introduce the method, a precursor solution for TiO<sub>2</sub> deposition was prepared by diluting the 12% TiCl<sub>3</sub> solution in deionized water with a ratio of 1:20. Then, the solution was neutralized to the pH 2.45  $\pm$  0.03 by slow addition of 0.6 M NaHCO<sub>3</sub> solution. The electrodeposition was performed by applying 64 mV vs Ag/AgCl (3 M KCl) on a Pt UME immersed in a freshly prepared TiCl<sub>3</sub> solution. The TiO<sub>2</sub> coverage ( $\theta_{TiO2}$ ) of TiO<sub>2</sub>@Pt is calculated from the difference in hydrogen underpotential deposition charges before and after electrodeposition of TiO<sub>2</sub>.

#### **3.3.5.** Fit for CV data to the BV model

CV was converted to overpotential-current data by taking the potential of the minimum current as an equilibrium potential. Exchange current ( $i_0$ ) and  $\alpha$  were respectively calculated from the y-intercept of the Tafel plot and the Tafel slope. Then, the data was fitted to the BV model using  $i_0$  and  $\alpha$ . The steady-state mass transport limited BV equation was used for the Fig. 2b, and the BV equation without mass transport limit,  $i = i_0 [e^{(1-\alpha)f\eta} - e^{-\alpha f\eta}]$ , was used for the Fig. 3.

#### **3.3.6.** Electrochemical Impedance Spectroscopy

A Gamry potentiostat was used for measuring impedance spectra of electrode– MEPBr<sub>2n+1</sub> interfaces. Pt UME or TiO<sub>2</sub>@Pt UME dipped in MEPBr<sub>2n+1</sub> served as a working electrode. The reference electrode was the Pt macroelectrode which was working electrode during MEPBr<sub>2n+1</sub> synthesis (see **Figure 3-1a**). The EIS experiments were carried out at different working electrode dc potentials superimposed by an ac potential of 5 mV rms. The frequency range was extended from 1 kHz to 500 kHz with 10 points per decade. The impedance spectra were fitted to the Randles circuit with spherical diffusion Warburg using the MEISP software.<sup>[97]</sup>

## 3.4. Results and Discussion

#### 3.4.1. Ultrafast Mass Transport System of MEPBr<sub>2n+1</sub>

A MEPBr<sub>2n+1</sub> droplet was electrochemically synthesized in a 250 mM solution of MEPBr in 1 M aqueous potassium phosphate buffer at a Pt macroelectrode (1.2 V vs Ag/AgBr (3 M KBr)).<sup>[97]</sup> Under these conditions, Br<sub>2</sub> is generated at the Pt electrode, following that it is captured by MEPBr in the solution to produce the MEPBr<sub>2n+1</sub>, which is immiscible with water to form a droplet:<sup>[99]</sup>

$$2Br^{-}(\mathrm{aq}) \rightleftharpoons Br_{2}(aq) + 2e^{-} \tag{3-1}$$

$$MEPBr(aq) + nBr_2(aq) \rightleftharpoons MEPBr_{2n+1}(IL)$$
(3-2)

The MEPBr<sub>2n+1</sub> droplet was immobilized on the Pt surface. The potential was held constant at the Pt electrode for several hours until the droplet became large enough to be observed by the naked eye.

MEPBr<sub>2n+1</sub> is composed of polybromides,  $Br_{2n+1}^-$ , i.e.  $Br_3^-$ ,  $Br_5^-$ , and  $Br_7^-$  that can be confirmed by Raman spectroscopy.<sup>[97]</sup> In MEPBr<sub>2n+1</sub>, the redox centers are highly concentrated, and MEP<sup>+</sup> and  $Br_{2n+1}^-$  can act as both electrolyte and solvent. MEPBr<sub>2n+1</sub> stores a very high concentration (7.5 M) of  $Br^-$ .<sup>[100]</sup>The apparent diffusion coefficients of redox species in MEPBr<sub>2n+1</sub> measured by EIS are surprisingly high,  $6 \times 10^{-4}$ – $3 \times 10^{-3}$  cm<sup>2</sup>/s.<sup>[97]</sup> This is two to three orders of magnitude higher than those of the species in aqueous solutions.

 $Br_{2n+1}^{-}$  has weak coordinate bonds between  $Br^{-}$  and  $Br_2$ , which is called halogen bonding (dashed line in **Figure 3-2a**), and  $Br^{-}$ ,  $Br_2$ , and  $Br_{2n+1}^{-}$  are at equilibrium in polybromide ILs:<sup>[101]</sup>

$$Br_{2n+1}^{-}(IL) \rightleftharpoons nBr_2(IL) + Br^{-}(IL)$$
 (3-3)

The facile dissociation and reconstitution of halogen bonding facilitate MT of Br<sub>2</sub>,



b Chemical Equilibrium

 $Br_{2n+1}^{-} \implies Br^{-} + nBr_{2}$ 

c Hopping transport



**Figure 3-2.** Ultrafast Mass Transport System of Br<sub>2</sub> within MEPBr<sub>2n+1</sub>. (a) Molecular structure of  $Br_{2n+1}^{-}$ .<sup>[102]</sup> Dashed lines represent halogen-bonding. (b) Chemical equilibrium between  $Br_{2n+1}^{-}$  and  $Br^{-}$  and  $Br_{2}$ . (c) Grotthuss-like mechanism of  $Br_{2}$  hopping transport. (d) Schematic representation for ultrafast MT system of  $Br_{2}$  within MEPBr<sub>2n+1</sub>.

Br<sup>-</sup>, and Br<sub>2n+1</sub><sup>-</sup>. **Figure 3-2** shows the mechanism proposed for the fast MT of Br<sup>-</sup> and Br<sub>2</sub> in MEPBr<sub>2n+1</sub> when Br<sub>2</sub> is electrochemically reduced. The equilibrium among Br<sup>-</sup>, Br<sub>2</sub>, and Br<sub>2n+1</sub><sup>-</sup> buffers the Br<sub>2</sub> concentration gradient near the electrode (**Figure 3-2b**). Br<sub>2</sub> elimination from Br<sub>2n+1</sub><sup>-</sup>, with a higher n, needs lower energy.<sup>[103]</sup> Since MEPBr<sub>2n+1</sub> contains high concentrations of Br<sub>2n+1</sub><sup>-</sup> and Br<sup>-</sup>, it can minimize the depletion of redox species at the electrode surface caused by the Faradaic reaction. In addition, Br<sub>2</sub> is deemed to transport through the Grotthuss-like hopping mechanism via the bromine network within the polybromide IL (**Figure 3-2c**).<sup>[104–107]</sup> Owing to the hopping transport, the species appears to move a long distance, although the actual displacement is small. The apparent diffusion coefficient of the redox species in MEPBr<sub>2n+1</sub> is actually higher than that of proton hopping so that the bromine reduction in MEPBr<sub>2n+1</sub> should be kinetically controlled even when a large overpotential,  $\eta$ , is applied to the electrode. Overall, the literature strongly implies that the MT in polybromide IL is extraordinarily fast.



3.4.2. Verifications of Electron Transfer Kinetic Controlled Current

**Figure 3-3. Voltammograms of MEPBr**<sub>2n+1</sub>. (a) CVs at the Pt UME and carbon UME of diameters 10  $\mu$ m and 11  $\mu$ m, respectively, in MEPBr<sub>2n+1</sub> (pH 3, phosphate buffer). Scan rate is 10 mV/s. (b) Comparison of the CV of the carbon UME in MEPBr<sub>2n+1</sub> (pH 3, phosphate buffer) and the voltammogram predicted from Equation (3-5). (c-d) CVs at Pt UMEs of diameters 10, 25 and 50  $\mu$ m in MEPBr<sub>2n+1</sub> (pH 3, phosphate buffer). Scan rate is 10 mV/s. Current is divided by (c) Electrochemically active surface area (ECSA) of Pt electrodes calculated from H<sub>upd</sub> voltammogram, and (d) geometric radius of UME.

A polycrystalline Pt UME or carbon UME was dipped in the electrochemically synthesized MEPBr<sub>2n+1</sub> droplet (**Figure 3-1a**). Fig. 2a shows the CVs of Br<sub>2</sub> reduction at the Pt UME and carbon UME. The reduction in MEPBr<sub>2n+1</sub> involves an inner-sphere electrochemical reaction of Br<sub>2</sub> to generate Br<sup>-</sup>:

$$Br_2(IL) + 2e^- \rightleftharpoons 2Br^-(IL) \tag{3-4}$$

Since  $Br_2$  reduction proceeds at the UME in a polybromide droplet having excess  $Br_2$  for only a short time, the electrochemical measurements do not cause significant perturbation to the composition of the polybromide IL. There was no side reaction such as the hydrogen evolution reaction in this potential range (**Figure 3-4**). Once the droplet was sufficiently large, the CVs were independent of its size. The CVs were also identical regardless of whether the reference electrode was located in the droplet or in the aqueous solution outside the droplet (**Figure 3-1b**). This shows that the impedance of the interface at MEPBr<sub>2n+1</sub> droplet/aqueous solution as well as that of aqueous solution was negligible.



**Figure 3-4.** CVs at Pt UME in 250 mM MEPBr, pH 3, 1 M potassium phosphate buffer solution at 100 mV/s (blue) and in  $MEPBr_{2n+1}$  which was electrochemically synthesized in 250 mM MEPBr, pH 3, 1 M potassium phosphate buffer solution at 10 mV/s (red).

The CV of Br<sub>2</sub> reduction shows a steady-state current ( $i_{ss}$ ) at a high  $\eta$  regardless of the electrode material (**Figure 3-3a**). In common electrochemical systems,  $i_{ss}$  usually originates from the restricted supply of reactants: (i) spherical diffusion-limited steady-state current at the UME, (ii) slow adsorption of reactants on the electrode for adsorption-coupled electron transfer, or (iii) a slow homogeneous chemical reaction that produces reactants of an electrochemical reaction.

First, the current coming from  $Br_2$  reduction is not governed by MT. The MT-limited voltammogram of the UME is sigmoidal, indicating the current-voltage relationship for a cathodic  $\eta$ :

$$i/_{i_0} = \left(1 - i/_{i_{SS,c}}\right)e^{-\alpha f\eta}$$
 (3-5)

Here,  $i_0$  is the exchange current,  $i_{ss,c}$  is the MT-limited steady-state current for the cathodic reaction,  $\alpha$  is the transfer coefficient, and f = F/RT. For reduction, the anodic contribution of the cathodic branch is negligible at high  $\eta$ . Figure 3-3b shows a comparison between the experimental CV and a simulated CV at the carbon UME based on Equation (3-5);  $i_0$ , and  $\alpha$  are calculated from the Tafel plot (Table 3-1). Significant differences between these voltammograms indicate that Br<sub>2</sub> reduction on

**Table 3-1.** Tafel slope, exchange current, and transfer coefficient extracted from the Tafel plot of Pt UME and carbon UME (N = 4).

	Pt UME	Carbon UME
Tafel slope (mV/decade)	$139\pm5$	$113\pm13$
Exchange Current, $i_0$ (nA)	$777\pm207$	$3.78\pm0.64$
Transfer coefficient, $\alpha$	$0.43\pm0.02$	$0.53\pm0.06$

the carbon UME cannot be explained by the MT limiting current. Moreover, comparison of the CVs of Br<sub>2</sub> reduction at Pt UMEs of different diameters in Figure **3-3c** suggests that Br<sub>2</sub> reduction on Pt is not governed by MT. If the current of UME is limited by MT, one should observe different  $\eta$  at which the current reaches plateau,  $i_{ss}$ , according to the geometric radius of the electrodes.<sup>[108]</sup> This is because the time for transition from planar diffusion to spherical diffusion depends on the electrode radius when a MT limiting current flows at the UME. However, the shapes of the voltammogram for the Pt UMEs are identical regardless of the geometric diameter of the UMEs. In addition, *i*<sub>ss</sub> at the Pt UME is regardless of its radius (Figure 3-3d), which is not in agreement with that the MT-limited  $i_{ss}$  should be proportional to the geometrical radius of the electrode.<sup>[108]</sup> Instead, currents in Figure 3-3c are proportional to the electrochemically active surface area (ECSA) of the electrodes, which is calculated from the charges of the hydrogen underpotential deposition  $(H_{upd})$ in potassium phosphate buffer. These experimental results confirm that the rates of  $Br_2$  reduction in the MEPBr<sub>2n+1</sub> droplet at the carbon and Pt UMEs are not restricted by MT, even over a wide range of  $\eta$  (-0.7 V or more negative).

Br<sub>2</sub> reduction is composed of elementary steps: Heyrovsky step, Volmer step, and Tafel step. Its mechanism differs depending on the reaction conditions, such as the reactants, solvents, and electrodes.<sup>[109–111]</sup> If the rate-determining step (rds) is the Tafel step (ex.  $Br_2 \rightarrow 2Br_{ad}$ ), the adsorption rate of redox species at the electrode surface should govern overall Br<sub>2</sub> reduction rate, resulting in  $i_{ss}$ .<sup>[112]</sup> However, the current is not likely to be limited by the adsorption because Br<sub>2</sub> adsorption on Pt is fast enough.<sup>[113–115]</sup>

It is widely accepted that the dissociation of  $Br_{2n+1}^{-}$  to  $Br_2$  and  $Br^{-}$  is fast enough not to restrict the  $Br_2$  reduction current.<sup>[109,116]</sup> In experiments, the voltammograms of  $Br_2$  reduction vary sensitively with changes in the surface structures of the electrodes. This can hardly occur when a homogeneous chemical reaction is rds.

# 3.4.3. Application of the MHC Model to Electron Transfer Kinetics at Pt and Carbon Electrode

A series of evidence consistently tell that  $i_{ss}$  in MEPBr<sub>2n+1</sub> is not controlled by mass transport, adsorption, or chemical reaction. On the other hand, Br<sub>2</sub> reduction CVs on the Pt and carbon UME are fitted well to the MHC model, suggesting that the current is governed by the ET kinetics.

The MHC model is an ET kinetics model that incorporates energy distributions of electrons in electrodes and electrolytes into the Marcus theory of heterogeneous ET.<sup>[93,117]</sup> **Figure 3-5a** illustrates the principle of the MHC model. The distribution of occupied electronic states in the electrode, g(E), follows the Fermi-Dirac equation and the energy levels of electrons in the redox-active species of electrolytes vary with the degree of stabilization by solvation. The electron energy distribution of these species can be represented by a probability density function W(E), which is a function of  $\lambda$ . In the case of reduction, an ET can occur from an occupied state in the electrode to the LUMO that has corresponding energy. Thus, the rate constant of an electrochemical reduction is proportional to the integral of the product of the number of occupied states in the electrode and W(E) of LUMOs of redox-active species along the electron energy level:<sup>[117,118]</sup>

$$k_{red/ox}^{MHC}(\eta) = Z \int_{-\infty}^{\infty} \exp\left(-\frac{(x - \lambda \pm e(E - E^0))^2}{4\lambda k_B T}\right) \frac{1}{1 + \exp(x/k_B T)} \, dx \quad (3-6)$$

Here,  $k_{red/ox}^{MHC}$  is rate constant of heterogeneous ET in the MHC model, Z is the preexponential factor accounting for the electronic coupling and the electronic density



Figure 3-5. Fitting the voltammograms to the Marcus-Hush-Chidsey model. (a) Electronic level diagram of the electrode-electrolyte interface in the MHC model. Relationship between heterogeneous electron transfer rate and electronic states at an electrode-electrolyte interface in the case of reduction is shown. y-axis is the energy, E.  $E_F$ ,  $E_0$  and V are Fermi level, formal potential, electrode potential respectively. The bell curve represents  $W_O(E)$  of LUMOs of redox-active species.  $k_{red}^{MHC}$  is proportional to the overlapped area of the number of occupied states in the electrode (yellow) and unoccupied states in redox-active species (blue).  $k_{red}^{MHC}$  reaches half of the maximum when  $-\Delta G^0$  for electron transfer is equal to  $\lambda$ . (b-c) Normalized Tafel plots for Br<sub>2</sub> reduction in the MEPBr<sub>2n+1</sub> with pH 3 phosphate buffer at (b) Pt UME, and (c) carbon UME. Experimental data (black dots) are compared to the fitting results of the MHC model (red lines) and the Butler-Volmer model (blue lines).

of states of the electrode, x is the energy, e is the elementary charge, and  $k_{\rm B}$  is the Boltzmann constant. According to the MHC model, when  $\lambda$  reaches certain value,  $k_{red/ox}^{MHC}$  does not increase with  $\eta$  because there is no corresponding W(E) at high E. This can cause ET kinetics-limited  $i_{ss}$ . ET-limited  $i_{ss}$  normalized to  $i_0$  depends  $\eta$ .<sup>[118]</sup>  $\eta$  reaching ET-limited  $i_{ss}$  increases with  $\lambda$ .

**Figure 3-5b, c** shows the Tafel plots for  $Br_2$  reduction in MEPB $r_{2n+1}$  at the

Pt UME and carbon UME (black dots) and the fits of these plots to the Butler-Volmer model (blue line) and MHC model (red line). The current–overpotential equation of the MHC kinetics derived from Equation (3-6) was utilized to fit the experimental data to the MHC model. Details on the derivation of the current-overpotential equation are described in **3.7. Appendix**. The experimental data agree well with the MHC model, revealing  $\lambda = 197$  and 379 meV for Pt UME and carbon UME, respectively. The Butler-Volmer model can explain the experimental data only for small values of  $\eta$ . Carbon UME has remarkably higher  $\lambda$  than that of Pt UME. Correspondingly, not only  $i_{ss}/i_0$  but also  $\eta$  reaching  $i_{ss}$  are larger at carbon than at Pt.

**Table 3-2.** Mean and standard deviation of reorganization energies of Pt UME measured in  $MEPBr_{2n+1}$  in 1 M phosphate buffers at pH 3 and 4.

	рН 3	pH 4
Reorganization energy (meV)	$196\pm21$	$197\pm13$

**Table 3-2** lists the  $\lambda$  values of Pt UMEs in buffers of different pHs on which  $\lambda$  was not dependent noticeably. In the microscopic ET theory,  $\lambda$  includes reorganization not only of solvents (outer-sphere reorganization energy,  $\lambda_0$ ) but also of redox species (inner-sphere reorganization energy,  $\lambda_i$ ). Since Br<sub>2</sub> reduction involves bromide adsorption on the electrode,  $\lambda$  may be associated with  $\lambda_i$  through changes in the bond length between bromide and the electrode during ET. The binding strength of Pt to bromide should be influenced by the solution pH,<sup>[119]</sup> and the MEPBr<sub>2n+1</sub> droplet has a significant water content because even hydrophobic ILs are known to contain water when surrounded by an aqueous solution.<sup>[88]</sup> But the experimental  $\lambda$  of Pt was not sensitive to pH notwithstanding. It tells that variation

in Pt-Br binding strength with pH change affects reorganization energy within a limited range. Hence the contribution of  $\lambda_i$  to  $\lambda$  is deemed to be negligible in this system.

**Table 3-3.** Mean and standard deviation of reorganization energies of Pt UME measured in  $MEPBr_{2n+1}$  and  $MBPBr_{2n+1}$  at pH 3, 1 M phosphate buffers. T test with unequal variances leads that two datasets have none-equal averages in 90 % confidence level.

	MEPBr <sub>2n+1</sub>	MBPBr <sub>2n+1</sub>
Reorganization energy (meV)	$196 \pm 21 \ (n = 32)$	$186 \pm 17 \ (n = 18)$

Considering that Br<sub>2</sub> reduction is an inner-sphere reaction occurring in IHP,  $\lambda_{o}$  should reflect the structure of the IHP. It is widely accepted that  $\lambda$  of solvating medium is the most crucial factor for  $\lambda_0$  not only in dilute electrolytes, <sup>[15,16,26,83,120]</sup> but also in RT-IL.<sup>[121–123]</sup> Several theoretical studies have proposed that  $\lambda_0$  is inversely proportional to  $\varepsilon$  in RT-IL.<sup>[121–123]</sup> In ionic liquids, the redox species are mainly surrounded by ions rather than solvents.<sup>[124,125]</sup> Hence, polarizabilities of ions should be important for  $\varepsilon$ . Table 3-3 compares reorganization energies of MEPBr<sub>2n+1</sub> and MBPB $r_{2n+1}$ . As predicted, the reorganization energy is smaller in MBPB $r_{2n+1}$  which has higher cation polarizability.<sup>[126]</sup> It is worth noting that interpretation of the reorganization energy of IHP as a part of EDL structure needs further study. Current reorganization energy models of RT-IL are derived from the Debye-Hückel theory,<sup>[121–123]</sup> which is based on the polarization of diluted electrolytes.<sup>[127,128]</sup>. But very strong Coulomb interactions among ions make the dielectric contribution of ILs complex. For example, hysteresis of potential-dependent EDL structure of ILs has been reported,<sup>[129-131]</sup> which may be associated with ultraslow capacitive process of IL.<sup>[132,133]</sup> Changes of the effective dielectric constant of IHP medium may alter the

potential gradient between the nominal plane of the electrode and IHP.<sup>[134]</sup>

#### **3.4.4.** Effect of Electrode Surface Charge on the Reorganization Energy



**Figure 3-6.**  $H_{upd}$  voltammogram at bare Pt and TiO<sub>2</sub>@Pt UMEs ( $\theta_{TiO2} = 0.25$ ) in 1 M aqueous potassium phosphate buffer (pH 3) recorded at a scan rate of 250 mV/s. The reference electrode was a mercury-mercurous sulfate electrode (MSE).

To examine the intrinsic electrode properties affecting  $\lambda$ , bare Pt was compared to surface-modified Pt. TiO<sub>2</sub> is a suitable material for surface modification because it acts as a passive layer that minimizes the effects on electrochemical reaction; moreover, it is chemically inert under the present experimental pH and potential. TiO<sub>2</sub> was electrodeposited on the Pt UME using a previously reported method.<sup>[98]</sup> The  $\theta_{TiO2}$  of the TiO<sub>2</sub>-modified Pt electrode (TiO<sub>2</sub>@Pt) was calculated by comparing the H<sub>upd</sub> values before and after electrodeposition (**Figure 3-6**).



**Figure 3-7.** (a–b) Normalized Tafel plots of TiO<sub>2</sub>@Pt with various  $\theta_{TiO2}$  in MEPBr<sub>2n+1</sub> at (a) pH 3 and (b) pH 4. Experimental data (markers) are compared to the fitting results of the MHC model (lines).

**Figure 3-7** show the normalized Tafel plots of bare Pt and TiO<sub>2</sub>@Pt UMEs in the MEPBr<sub>2n+1</sub> droplet synthesized at pH 3 and pH 4, respectively. The  $\lambda$  of TiO<sub>2</sub>@Pt increases with  $\theta_{TiO2}$  at pH 3, while no remarkable changes were observed at pH 4. The pH dependency of TiO<sub>2</sub>@Pt should be ascribed to the surface charge of TiO<sub>2</sub> because the isoelectric point of TiO<sub>2</sub> is pH 4–5;<sup>[135,136]</sup> thus, the net surface charge of TiO<sub>2</sub> is positive at pH 3 and almost zero at pH 4. Accordingly, the surface charge of Pt does not change significantly with pH because halides suppress the formation of Pt oxide. Introducing charges on the electrode surface will alter the ionic composition of the IHP in the IL. The EDL of an IL is very compact because of its extremely high ionic strength; most of the charges at the electrode surface are compensated in the IHP. When the electrode surface is positively charged, Br<sup>-</sup> anions, which have a higher charge density than other anions in MEPBr<sub>2n+1</sub>, are likely to occupy the IHP to compensate for the surface charges. When the electrode is less positively charged, the MEP cations compensate for these charges proportionately. The polarizabilities of quaternary ammonium cations (10–20) are higher than that of Br<sup>-</sup> (5.8).<sup>[137]</sup> Accordingly, the IHP medium of TiO<sub>2</sub>@Pt should be less polarizable at pH 3. Such trend should be more manifest at higher  $\theta_{TiO2}$ . The  $\lambda$  value of TiO<sub>2</sub>@Pt at pH 4 is independent of  $\theta_{TiO2}$ , and almost zero charge of TiO<sub>2</sub> accounts for that. It is difficult to evaluate the  $\lambda$  value of TiO<sub>2</sub>@Pt at pH 2 or less because TiO<sub>2</sub> is not stable at such low pH. In addition, the synthesis of polybromide IL from an aqueous solution of MEPBr above pH 5 is accompanied by bromate formation, which can significantly change the composition of MEPBr<sub>2n+1</sub>.



**Figure 3-8. EIS analysis of Pt and TiO**<sub>2</sub>@Pt in MEPBr<sub>2n+1</sub>. (a) Representative Nyquist plot of Pt UME in MEPBr<sub>2n+1</sub> (red dots, frequency decreases from left to right) and its fit to the Randles circuit with spherical diffusion Warburg (black line). The left semicircle shows the charge transfer resistance and double layer capacitance. (b-d) The fitted double-layer capacitance ( $C_{dl}$ ) as a function of electrode dc potentials at (b, d) Pt UME and (c, e) TiO<sub>2</sub>@Pt with a  $\theta_{TiO2}$  of 0.55 in MEPBr<sub>2n+1</sub> at (b-c) pH 3 and (d-e) pH 4.

EIS analyses at Pt and TiO<sub>2</sub>@Pt in MEPBr<sub>2n+1</sub> was performed to supports the pH dependent PZC of Pt and TiO<sub>2</sub>@Pt UME in MEPBr<sub>2n+1</sub>. The EIS data was fitted to the Randles circuit with spherical diffusion Warburg.<sup>[97]</sup> EIS has been employed to measure PZC of electrodes in ionic liquids.<sup>[129,130,138]</sup> EDL structure of ionic liquids cannot be explained by classical Gouy–Chapman–Stern theory which predicts the minimum  $C_{dl}$  at PZC in diluted solution. Alternatively, ionic liquids have local maximum  $C_{dl}$  around PZC because crowded ions in the EDL of ionic liquids block further charging.<sup>[139]</sup> Correspondingly,  $C_{dl}$ –E of Pt and TiO<sub>2</sub>@Pt in MEPBr<sub>2n+1</sub> in **Figure 3-8** have bell-shaped curve while the potential of local maximum  $C_{dl}$  is assigned to PZC. PZC of Pt UME is 1.05 V in both MEPBr<sub>2n+1</sub> at pH 3 and pH 4, and PZC of TiO<sub>2</sub>@Pt ( $\theta_{TiO2}$ ) is 0.55 V and 0.85 V in MEPBr<sub>2n+1</sub> at pH 3 and pH 4, respectively.

The experimental results from TiO<sub>2</sub>@Pt corroborate how electrode surface charge influences  $\lambda$ , which can explain the high  $\lambda$  of carbon compared to that of Pt. Being consistent with the work function and nonspecific adsorption of Br<sup>-</sup>, the PZC of carbon is more negative than that of Pt.<sup>[140]</sup> Hence Br<sup>-</sup> is more probable in IHP so that the medium in it should be less polarizable. It suggests that the net dielectric constant of the electrolytes around the carbon would be lower.

To date majority of research has been addressing electrocatalytic activity mostly in terms of the adsorption on the electrode materials based on the Sabatier's principle.<sup>[59,141,142]</sup> However, the community increasingly realizes it is insufficient to understand the electrocatalysis relying on the adsorption descriptor only.<sup>[18]</sup> In line with a few recent approaches, our report here supports that the properties of electrode material give rise to characteristic change in the reaction environment of the liquid phase in vicinity to the electrode surface, significantly influencing to electrocatalytic current.

# 3.5. Conclusion

RT-ILs have emerged as promising electrolytes for electrocatalytic reactions.<sup>[84,85]</sup> Water-in-salt electrolytes, which are attracting significant interests owing to their potential applications in batteries<sup>[143]</sup> and electrocatalysis,<sup>[144]</sup> have EDL structures similar to those of RT-ILs.<sup>[145]</sup> In this study, the reorganization energy of Br<sub>2</sub> reduction was evaluated in a RT-IL, MEPBr<sub>2n+1</sub>, which has an incredibly high diffusion coefficient for Br<sup>-</sup> and Br<sub>2</sub>. A distinct kinetically controlled steady-state current was observed at a high overpotential, and the Br<sub>2</sub> reduction voltammogram could be successfully fitted to the MHC model. The reorganization energy as obtained for Br<sub>2</sub> reduction is sensitive to the surface charges of the electrode. This can be explained by the polarizability of the IHP, which dramatically varies with the surface charges. As demonstrated in this work, polybromide RT-ILs can serve as a model system not only for RT-ILs but also for water-in-salt electrolytes, in order to understand the electrocatalytic activities related to the EDL structure. Employing MEPBr<sub>2n+1</sub> RT-IL, one could investigate how a variety of electrode surfaces, including electrode materials and surface modifications other than TiO<sub>2</sub>, affect microscopic environment within IHP so as to understand given heterogeneous electron transfer kinetics. We believe that the findings of this work will provide new insights into the design of electrocatalysts.

In future research, a wide range of cations with different polarizabilities will be employed in the polybromide IL to collect more evidences for the dependence of reorganization energy on the polarizabilities of the solution. In addition, computational studies about the polybromide-electrode interface could help with evaluating quantitative contribution of the outer-sphere reorganization energy and the inner-sphere reorganization energy, respectively.

# 3.6. Acknowledgements

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# 3.7. Appendix: Derivation of the Current-Overpotential Equation for the simplified MHC Model

Since the electrochemical rate constant for the MHC model in Equation (3-6) is mathematically difficult to be employed, Bazant *et al.* reported an analytical approximation of the equation. A reduction rate constant,  $k_{red}$  and an oxidation rate constant,  $k_{ox}$  in the simple formula for the MHC model is expressed as follows when  $\lambda^* \gg 1$ :<sup>[117]</sup>

$$k_{red}(\lambda^*, E^*) = Z \cdot \frac{\sqrt{\pi\lambda^*}}{1 + \exp(E^* - E^{0,*})} \cdot \operatorname{erfc}\left(\frac{\lambda^* - \sqrt{1 + \sqrt{\lambda^*} + (E^* - E^{0,*})^2}}{2\sqrt{\lambda^*}}\right)$$
(3-7)  
$$k_{ox}(\lambda^*, E^*) = Z \cdot \frac{\sqrt{\pi\lambda^*}}{1 + \exp(-(E^* - E^{0,*}))} \cdot \operatorname{erfc}\left(\frac{\lambda^* - \sqrt{1 + \sqrt{\lambda^*} + (E^* - E^{0,*})^2}}{2\sqrt{\lambda^*}}\right)$$
(3-8)

where  $\lambda$  is reorganization energy, *E* is the electrode potential,  $E^0$  is the standard potential, *Z* is the pre-exponential factor, and the superscript \* denotes normalization to the thermal voltage as shown in Equation (3-9).

$$\lambda^* = \frac{\lambda}{k_B T} \tag{3-9}$$

where,  $k_B$  is the Boltzmann constant, and T is temperature.

However, the simple formula suggested by Bazant *et al.* cannot be directly applied to fit the experimental data because both Z and  $E^0$  of Br<sub>2</sub> reduction in MEPBr<sub>2n+1</sub> are unknown. Thus, we constructed a current-overpotential equation for the MHC model along coordinates of current normalized by exchange current  $({}^{i}/{i_0})$  and overpotential ( $\eta = E - E_{eq}$ ).

According to Faraday law, the current for one electron-transfer is as follows:

$$\frac{i(E)}{FA} = k_{ox}C_R - k_{red}C_O \tag{3-10}$$

where  $C_i$  is the concentration of redox-active species, F is Faraday constant, and A is electrode surface area. Assuming that the rate-determining step for the current is not mass transport of redox-active species, but electron transfer between electrodeelectrolyte interface, concentrations of redox-active species at the electrode surface are the same as those in the bulk. Under this condition, the Nernst equation is expressed as follows:

$$E_{eq} = E^0 - \frac{RT}{F} \ln \frac{C_R}{C_O}$$
(3-11)

Let  $c^* = (E_{eq} - E^0) \cdot F /_{RT} = E_{eq}^* - E^{0,*},$ 

$$\frac{C_o}{C_R} = \exp(c^*) \tag{3-12}$$

Substituting Equation (3-7), (3-8), and (3-12) into equation (3-10) yields Equation (3-13).

$$\frac{i(E)}{ZFAC_R}$$

$$=\sqrt{\pi\lambda^*} \cdot \operatorname{erfc}\left(\frac{\lambda^* - \sqrt{1 + \sqrt{\lambda^*} + (\eta^* + c^*)^2}}{2\sqrt{\lambda^*}}\right) \left(\frac{\exp(\eta^*) - 1}{\exp(\eta^*) + \exp(-c^*)}\right)$$
(3-13)

where  $\eta^* = \eta \cdot \frac{e}{k_B T} = (E^* - E^{0,*})$ . *e* is the elementary charge

Exchange current can be expressed as follows:

$$\frac{i_0}{ZFAC_R} = \operatorname{erfc}\left(\frac{\lambda^* - \sqrt{1 + \sqrt{\lambda^*} + c^{*2}}}{2\sqrt{\lambda^*}}\right) \left(\frac{\sqrt{\pi\lambda^*}}{1 + \exp(-c^*)}\right)$$
(3-14)

Organizing Equation (3-13) and (3-14) yields Equation (3-15) which is the currentoverpotential equation for the MHC kinetics.

$$\frac{i(E)}{i_0} = \frac{\operatorname{erfc}\left(\frac{\lambda^* - \sqrt{1 + \sqrt{\lambda^*} + (\eta^* + c^*)^2}}{2\sqrt{\lambda^*}}\right)}{\operatorname{erfc}\left(\frac{\lambda^* - \sqrt{1 + \sqrt{\lambda^*} + c^{*2}}}{2\sqrt{\lambda^*}}\right)} \left(\frac{\exp(\eta^*) - 1}{\exp(\eta^*) + \exp(-c^*)}\right)(1 + \exp(-c^*))$$
(3-15)

Reorganization energy was calculated by fitting  $\log(i/i_0)$  vs  $\eta$  data from 0 V to -0.6 V vs  $E_{eq}$  to equation (3-15) using MATLAB with fitting parameters of  $\lambda^*$  and  $c^*$ .  $i_0$  was calculated using the Tafel plot analysis.  $\lambda$  of this work ( $\lambda^*$  higher than 7.5) is large enough to satisfy the assumption of the simple formula for the MHC model.

# Chapter 4. Reorganization Energy in a Polybromide Ionic Liquid Measured by Scanning Electrochemical Cell Microscopy

Herein, we employ SECCM to evaluate the reorganization energy for  $Br_2$  reduction. This technique enables the investigation of reorganization energies on complex alloy surfaces, such as high-entropy alloy, which are challenging to fabricate in the form of ultramicroelectrodes.

This chapter consists of a communication which has been published. I was responsible for the experimentation, data analysis, and paper preparation. Emmanuel B. Tetteh contributed to the design of the experiments and the instrumentation. Alan Savan, Bin Xiao, and Alfred Ludwig prepared the high-entropy alloy material-library. This work was supervised by Taek Dong Chung and Wolfgang Schuhmann.

# Reorganization Energy in a Polybromide Ionic Liquid Measured by Scanning Electrochemical Cell Microscopy

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### 4.1. Abstract

RT-ILs are promising electrolytes for electrocatalysis. Understanding the effects of the electrode-electrolyte interface structure on electrocatalysis in RT-ILs is important. Ultrafast mass transport of redox species in MEPBr<sub>2n+1</sub> enabled evaluation of the reorganization energy ( $\lambda$ ), which reflects the solvation structure in the IHP.  $\lambda$  was achieved by fitting the electron transfer rate-limited voltammogram at a Pt UME to the Marcus-Hush-Chidsey model for heterogeneous electron transfer kinetics. However, it is time-consuming or even impossible to prepare electrode materials including alloys of numerous compositions in the form of UME for each experiment. Herein, we report a method to evaluate the  $\lambda$  of MEPBr<sub>2n+1</sub> by SECCM, which allows high throughput electrochemical measurements using a single electrode with high spatial resolution. Fast mass transport in the nanosized SECCM tip is critical for achieving heterogeneous electron transfer-limited voltammograms. Furthermore, investigating  $\lambda$  on a HEA-ML composed of Pt, Pd, Ru, Ir, and Ag suggests a negative correlation between  $\lambda$  and the work function. Given that the potential of zero charge correlates with the work function of electrodes, this can be attributed to the surface-charge sensitive ionic structure in the IHP of MEPBr<sub>2n+1</sub>, modulating the solvation energy of the redox-active species in the IHP.

Keywords : Ionic liquids (ILs) • Scanning Electrochemical Cell Microscopy (SECCM) • Marcus-Hush-Chidsey model • Reorganization energy • High-entropy Alloy (HEA)

# 4.2. Introduction

RT-ILs are promising electrolytes for energy conversion and storage, such as in electrocatalysis,<sup>[84,146,147]</sup> batteries,<sup>[148]</sup> and supercapacitors<sup>[149]</sup> owing to their distinctive properties compared to typical solvents. The versatility of available structures of RT-IL ions allows the design of the appropriate structure of cations and anions for the desired electrocatalytic reaction<sup>[84,146,147]</sup> by adjusting the physical and chemical properties such as dielectric constant, thermal stability, conductivity, solubility, and electrochemical window.<sup>[150]</sup> RT-ILs have a complex EDL structure compared to conventional electrolytes because ions are strongly correlated to other ions or charged solid surfaces due to their extremely high ionic strength.<sup>[139]</sup> Therefore, the EDL structure of RT-ILs strongly depends on the surface charge of the electrode.<sup>[90]</sup> Since the EDL is where the electrochemical reactions occur, probing the reaction environment properties in the EDL according to the surface charge of the electrode is crucial for understanding the electrochemical activities of RT-ILs.

According to the Marcus theory,  $\lambda$  is the key parameter connecting the activation barrier for electron transfer and the microscopic structure of chemical species.<sup>[60]</sup> Solvation structure, thus the dielectric constant of solvents has a significant contribution to  $\lambda$ .<sup>[16]</sup> For example, the investigation of  $\lambda$  of the species in the EDL showed a lower static dielectric constant of solvents closer to the electrode.<sup>[26,83]</sup>  $\lambda$  can be obtained by fitting the electron transfer rate constant versus the applied potential to the MHC model (also called the Marcus-Gerischer model) representing the heterogeneous electron transfer kinetics. Electron transfer rate constants at various overpotentials can be determined from the voltammogram where the electron transfer kinetics at the electrode-electrolyte interface is slower than mass

transport of redox-active species. However, the low diffusion coefficient of species within typical RT-ILs, caused by their high viscosity,<sup>[139]</sup> can result in an extended mass transport-governed region. Recently, our group focused on a polybromide ionic liquid as an effective model system to measure  $\lambda$  in RT-ILs for exploring the role of the EDL structure of RT-ILs in electrochemical kinetics.<sup>[151]</sup> Hopping transports of both Br<sub>2</sub> and Br<sup>-</sup>through the polybromide chain network boost their mass transport so that the apparent diffusion coefficient of species in MEPBr<sub>2n+1</sub> were about  $6 \times 10^{-4}$  $-3 \times 10^{-3}$  cm<sup>2</sup> s<sup>-1</sup>, which is even faster than that of protons.<sup>[97]</sup> Voltammograms of MEPB $r_{2n+1}$  at Pt UME were dominated by the electron transfer kinetics in a wide range of overpotentials (until – 0.6 V) and were well-fitted to the MHC model.<sup>[151]</sup> Application of MEPBr<sub>2n+1</sub> to various electrode materials requires high-throughput experimentation for statistical validity; however, employing UME needs a lot of time and labor because only one set of experimental data can be obtained from a single electrode. Moreover, preparation of alloy UMEs with a variety of compositions is highly challenging and sometimes impossible compared to that of a single material. SECCM is a powerful technique enabling spatially resolved electrochemical measurements and easy data acquisition at multiple spots in one operation.<sup>[50-52]</sup> SECCM was used successfully to examine the structure-activity relationships at polycrystalline metal electrodes,<sup>[53,152]</sup> multigrain graphene electrodes,<sup>[153]</sup> nanoparticle-supported electrodes,<sup>[55]</sup> and HEA<sup>[154]</sup> by measuring not only electrocatalytic activities, but also Tafel slope,<sup>[53]</sup> using galvanostatic techniques,<sup>[155]</sup> and determining the PZC.<sup>[53]</sup> Despite the versatile ability of SECCM to access the measurement of various electrochemical parameters, SECCM has not been reported for the determination of  $\lambda$ .

Herein, we report a method to measure  $\lambda$  of MEPBr<sub>2n+1</sub> using SECCM by

comparing the voltammograms in MEPBr<sub>2n+1</sub> on polycrystalline Pt with respect to the SECCM tip diameters. It could be demonstrated that the voltammograms obtained with the different SECCM tips of several hundred nanometers diameter were not limited by diffusional mass transport, and hence entirely governed by the electron transfer kinetics. The voltammograms could be fitted to the MHC model for heterogeneous electron transfer kinetics, yielding a  $\lambda$  of 197 ± 4 meV for the polycrystalline Pt electrode. To identify the electrode material effects on RT-IL electrocatalysis, SECCM experiments were performed in MEPBr<sub>2n+1</sub> on a HEA-ML. This continuous composition spread thin film library comprises compositional gradients of the content of its constituents Pt, Pd, Ir, Ru, and Ag. A higher  $\lambda$  value was observed at HEA compositions with a smaller elemental composition-weighted average of the work function which correlates with a more negative PZC. Hence, the net dielectric constant of the solvating medium in the IHP, which is sensitive to the surface charge, has an important role in RT-IL electrocatalysts.

# 4.3. Experimental Methods

#### 4.3.1. Materials

1-ethyl-1-methylpyrrolidinium bromide (Sigma-Aldrich, MEPBr, >99 %), potassium phosphate monobasic (Sigma-Aldrich, KH<sub>2</sub>PO<sub>4</sub>, 99.7%), potassium phosphate dibasic (Riedel-de Haën, K<sub>2</sub>HPO<sub>4</sub>,  $\geq$ 98%) were used as received. All solutions were prepared with Milli-Q deionized water. A single crystal (100) Si wafer of 100 mm diameter with 1000 nm wet thermal SiO<sub>2</sub> as a barrier layer was used as a substrate for the Pt thin-film electrode and the HEA-ML. Metallic sputter targets with high purities were used for the deposition: Ag (purity 99.99%), Ir (purity 99.9%), Pd (purity 99.99%), Pt (purity 99.99%), and Ru (purity 99.95%). Single barrel quartz capillaries (0.9 mm 1.2 mm outer diameter and 10 cm length with filaments) were purchased from Sutter instrument.

#### 4.3.2. Fabrication of Electrodes

The polycrystalline Pt thin-film electrode was prepared by the sequential deposition of 20 nm Ti (adhesion layer) and 40 nm Pt on a 100 mm diameter Si (100) wafer by magnetron sputtering (DCA Instruments, Turku Finland). The deposition was done in Ar (99.9999%) at a pressure regulated to 0.67 Pa without additional intentional heating. The deposition rate was 0.3 nm/s. The same method was applied to fabricate the HEA-ML by co-sputtering from five single-element targets each oriented at an angle of 45° relative to the surface of a stationary sample located at the confocal point.<sup>[32]</sup> The target-to-substrate distance was 18.5 cm, and the five cathodes are equally spaced in a circle (72° apart), with this geometry resulting in nearly linear thickness gradients from each sputter source. The elemental composition of the prepared HEA-ML was determined by EDX with an acceleration voltage of 20 kV using a scanning electron microscope (JEOL 5800) and a silicon-drift detector (INCA Xact, Oxford Instruments).

#### **(b)** 10 (a) <sub>20</sub> 8 10 6 i (mA) *i* (mA) -10 2 -20 0 0.3 0.5 0.7 0.9 1.1 1000 2000 3000 0 4000 E (V vs. Ag/AgCl) t (sec)

#### 4.3.3. Synthesis of MEPBr<sub>2n+1</sub> Ionic Liquid

**Figure 4-1.** (a) Cyclic voltammogram on Pt surfaces in 1 M potassium phosphate buffer (pH 3) containing 250 mM MEPBr at a scan rate of 0.1 V/s. The arrow represents the direction of the scan. (b) Chronoamperogram on Pt surfaces at 1 V vs. Ag/AgCl (3 M KCl) in 1 M potassium phosphate buffer (pH 3) containing 250 mM MEPBr measured during the electrochemical synthesis for MEPBr<sub>2n+1</sub>.

MEPBr<sub>2n+1</sub> was electrochemically synthesized in a three-electrode system in 250 mM MEPBr, 1 M potassium phosphate aqueous buffer solution as previously reported.<sup>[97]</sup> A Ag/AgCl (3 M KCl) and a Pt wire were employed as a reference electrode and a counter electrode, respectively. A Pt film electrode was used as the working electrode, and the diameter of the Pt exposed to the solution was larger than 3 mm. The CV in MEPBr solution at the Pt electrode indicates that Br<sup>-</sup> oxidation occurs at the potentials higher than 0.8 V vs. Ag/AgCl (3 M KCl) (**Figure 4-1a**). Therefore, 1 V vs. Ag/AgCl (3 M KCl) was applied at the Pt electrode for several hours to oxidize Br<sup>-</sup> into Br<sub>2</sub>, and MEPBr subsequently captures the generated Br<sub>2</sub> to produce MEPBr<sub>2n+1</sub>, which is immiscible with water (**Figure 4-1b**). After the
synthesis, a dark orangish-brown  $MEPBr_{2n+1}$  droplet with several mm in size was observed.

#### 4.3.4. Electrochemical Measurements with SECCM

SECCM tips were prepared by pulling a single barrel quartz capillary. After careful cleaning a capillary with wipes soaked in a small amount of isopropanol, it was placed in the laser puller (P2000, Sutter). It was pulled with pulling parameters of HEAT 780, FIL 4, VEL 40, DEL 130, and PUL 100 to get the tip diameter in the hundred-nanometer scale. The diameter of the tip was measured by SEM (FEI Quanta 3D).

The synthesized MEPBr<sub>2n+1</sub> was carefully injected into the pulled capillary using MicroFil needles (World Precision Instruments). The injection should be slow enough that the end of the capillary is filled with MEPBr<sub>2n+1</sub> without any air bubbles. Then, the capillary was sequentially filled with MEPBr solution to cover the MEPBr<sub>2n+1</sub>. We inserted a Pt wire into the capillary from the back as a quasireference/counter electrode. The fast electron transfer reaction between Br<sub>2</sub> and Br<sup>-</sup> in MEPBr<sub>2n+1</sub> maintains the potential of the reference electrode.<sup>[97]</sup> It was assured that a sufficiently large portion of the Pt wire was in contact with MEPBr<sub>2n+1</sub>.

All electrochemical experiments were performed using a home-built SECCM workstation.<sup>[55]</sup> The relative location of the SECCM tip to the sample electrode surface was determined by controlling the electrode coordinate using an x,y,z-stepper motor (Owis) with a LStep PCIe (Lang) controller, and an x,y,z-piezo cube (P-611.3S nanocube, Physik Instrumente) with an analog amplifier (E-664, Physik Instrumente). The SECCM tip was coarsely placed about 20–50 µm above a region of interest on the sample electrode surface using the stepper motor controlled

positioning system, an optical camera (DMK 21AU04, The Imaging Source) and a cold light source (KL1500 LCD, Schott) before performing fine positioning and electrochemical measurements. Hopping-mode SECCM scan experiments consist of a fine approach of the tip using the z-piezo, electrochemical measurements, retraction of the tip from the surface and a lateral movement of the tip using the x- and y-piezos. The electrochemical cell was a 2-electrode system. The current flowing through the reference/counter electrode was measured using a variable gain transimpedance amplifier (DLPCA-200, FEMTO) and a variable gain voltage amplifier (DLPVA-100-B-S, FEMTO).

## 4.3.5. Fitting Methods to Obtain the Value of the Reorganization Energy from the CV Data

The SECCM data were processed using the MATLAB (Mathworks) software package.  $\lambda$  was obtained from the forward scan of the CVs. First, the equilibrium potential ( $E_{eq}$ ) was achieved by finding the potential having the minimum current in the Tafel plot. After that, the exchange current ( $i_0$ ) was calculated by fitting the forward scan of the CV to a linear equation in the overpotential ( $\eta$ ) range from – 50 mV to 50 mV. The slope of the linear fit multiplied by *RT/F* is  $i_0$ .  $\lambda$  was calculated by fitting the Tafel plot ( $\log(i/i_0)$  vs.  $\eta$ ) data from 0 V to – 0.6 V vs.  $E_{eq}$  to Equation (4-4) using MATLAB with one fitting parameter of  $\lambda$ .

### 4.4. Results and Discussions

## 4.4.1. Electron Transfer Kinetics Controlled-voltammograms Measured by SECCM



Figure 4-2. Schematic illustration of the SECCM electrochemical cell configuration for the electrochemical measurements in  $MEPBr_{2n+1}$ .

Polybromide  $(Br_{2n+1}^{-})$  with N-methyl-N-ethyl-pyrrolidinium (MEP<sup>+</sup>), i.e. MEPBr<sub>2n+1</sub>, is a redox-active ionic liquid because  $Br_{2n+1}^{-}$  can easily dissociate into  $Br_2$  and  $Br^{-}$ (Equation (4-1)) that can undergo a Faraday reaction (Equation (4-2)).<sup>[151]</sup>

$$Br_{2n+1}^{-} \rightleftharpoons Br^{-} + nBr_2 \tag{4-1}$$

$$Br_2 + 2e^- \rightleftharpoons 2Br^- \tag{4-2}$$

Electrochemically synthesized MEPBr<sub>2n+1</sub> contains Br<sub>3</sub><sup>-</sup>, Br<sub>5</sub><sup>-</sup>, and Br<sub>2n+1</sub><sup>-</sup>  $(n \ge 2)$ ,<sup>[97]</sup> as well as a high concentration of Br<sup>-</sup> (7.5 M).<sup>[100]</sup> Polybromide RT-ILs enable a fast supply of the reactant for Br<sub>2</sub> reduction because the equilibrium between Br<sub>2n+1</sub><sup>-</sup> and Br<sup>-</sup> and Br<sub>2</sub> (Equation (4-1)) buffers the Br<sub>2</sub> consumption near the electrode surface,<sup>[101]</sup> and both Br<sup>-</sup> and Br<sub>2</sub> can do hopping transport through the polybromide

chain network.<sup>[105,106]</sup> Moreover, the mass transport gets faster in the polybromide RT-ILs with higher chain lengths due to the smaller dissociation energy of  $Br_2$  from  $Br_{2n+1}^{-,[97,103]}$  Therefore, it is unsurprising that voltammograms for  $Br_2$  reduction in MEPBr<sub>2n+1</sub> at the Pt UME were not controlled by mass transport of  $Br_2$  but instead by electron transfer kinetics.<sup>[151]</sup>



**Figure 4-3.** Typical *i-t* curve measured during the approach of the SECCM tip filled with MEPBr<sub>2n+1</sub> to the Pt sample surface at 0.2 V vs. the Pt wire. The Z-axis approach of the tip was stopped when the current became higher than the preset current value.

**Figure 4-2** shows the SECCM configuration for the electrochemical experiments of MEPBr<sub>2n+1</sub>. First, the SECCM tip filled with MEPBr<sub>2n+1</sub> approached the substrate with a pre-defined bias, usually 0.2 V vs. the Pt wire, until the MEPBr<sub>2n+1</sub> droplet at the end of the SECCM tip touched the electrode surface. This led to a positive current spike (**Figure 4-3**), then CVs were carried out. **Figure 4-5** compares CVs of MEPBr<sub>2n+1</sub> on the Pt surface in dependence of the SECCM tip diameters. SEM images of the tips are shown in **Figure 4-4**. The CV measured with a 13.8 µm diameter capillary (**Figure 4-5a**) demonstrates the electrochemical behavior of MEPBr<sub>2n+1</sub> at the Pt electrode. Br<sup>-</sup> oxidation occurs at the potential (*E*) > 0 V while Br<sub>2</sub> reduction starts at the *E* < 0 V vs. the Pt wire. The cathodic current





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reached the plateau at -0.6 V and increased again at more negative E, indicating that there is a side reaction at E < -0.7 V. The observed large hysteresis between the forward and the backward scans implies that the CV was controlled by the masstransport flux of redox-active species. The CV measured with the SECCM tip with 1.85 µm diameter was nearly sigmoidal (Figure 4-4b). The hysteresis between the forward and the backward scans was smaller in the CV of the 1.85 µm diameter tip compared to that of the 13.8 µm diameter tip. This is due to the faster mass transfer in smaller diameter tips.<sup>[156,157]</sup> On the other side, CVs obtained with SECCM tips with hundreds of nanometers diameters (Figure 4-4c, d) exhibited clear sigmoidal shapes, with the forward scan and the backward scan being completely undistinguishable. Furthermore, the shapes of both voltammograms with the SECCM tips of 570 nm and 160 nm diameters were completely identical as shown in Figure 4-4e. Considering that the geometry of the tip is critical for determining the mass transport behaviors in SECCM experiments, the identical voltammogram shape regardless of the tip diameter supports a conclusion that they were not limited by the mass transport. The mass transport flux in SECCM increases with smaller tip diameter.<sup>[156]</sup> This phenomenon can be also found in the mass transport theory of the UME: the spherical diffusional flux at the UME is inversely proportional to the electrode radius.<sup>[60]</sup> The steady-state mass transport-limited current increases at the smaller UME, and besides, the half-wave potential  $(E_{1/2})$  as well as the potential reaching the steady-state is more far from the  $E_{eq}$ .<sup>[158,159]</sup> This is because the fast mass transport expands the kinetic regime in the voltammogram, causing  $E_{1/2}$  of the voltammogram to be delayed. Figure 4-4f demonstrates  $E_{1/2}$  calculated from the CVs of the various tip diameters.  $E_{1/2}$  shifted negatively in the SECCM tip diameters from 13.8  $\mu$ m to 570 nm, but  $E_{1/2}$  of the 160 nm diameter tip was comparable to that of the

570 nm although the mass transport should be faster in the 160 nm diameter tip. This corroborates that the CVs of the 570 nm and 160 nm SECCM tips were not controlled by the mass transport anymore, and rather controlled by the electron transfer kinetics. These voltammograms were well-fitted to the MHC model for heterogeneous electron transfer kinetics, which is further discussed in the next section.



4.4.2. Reorganization Energy at Polycrystalline Pt in MEPBr<sub>2n+1</sub>

Figure 4-6. A schematic diagram for the MHC model and typical fit results for exchange current ( $i_0$ ) and reorganization energy ( $\lambda$ ). (a) Electronic level diagram in the case of reduction according to the MHC model.  $E_F$  and  $E^{0'}$  are Fermi level and formal potential, respectively. The density of states of the electrolyte is the probability density function of the oxidized form of redox-active species. (b) Linear fit of MEPBr<sub>2n+1</sub> voltammogram on the Pt from the overpotential range of -50 mV to 50 mV. (c) Normalized Tafel plots for Br<sub>2</sub> reduction in MEPBr<sub>2n+1</sub> and the result of the MHC model fitting.

The MHC model combines the Marcus theory for the heterogeneous electron transfer kinetics, which is the Marcus-Hush theory (MH theory), and the distribution of electronic states in an electrode and electrolytes.<sup>[160]</sup> The key principle of the MHC model is that, e.g. in the case of reduction, the local electron transfer rate constant at each electronic state energy level is proportional to the density of states (DOS) of occupied states in the electrode and the DOS of the unoccupied electronic states in the redox-active species (Figure 4-6a). The Fermi-Dirac distribution describes the electronic states of the electrode while that of redox-active species is represented by the standard potential ( $E^0$ ) of the species and  $\lambda$ . The overall electron transfer rate constant across the electrode-electrolyte interface can be expressed by the integral of the local electron transfer rate over all the electronic states. The MHC model has successfully explained the potential-dependent electron transfer kinetics up to a high overpotential better than either the Marcus-Hush (MH) theory or the BV kinetics not only for simple one outer-sphere electron transfer<sup>[15]</sup> but also for the complex reactions.<sup>[14,16,24,25]</sup> One distinctive characteristic of the MHC model is that the electron transfer rate constant reaches a steady state at a sufficiently high overpotential, which is not predicted from the BV kinetics and the MH theory. This comes from the absence of the corresponding unoccupied states in the electrolytes when the Fermi level  $(E_F)$  of the electrode becomes higher than the electronic state levels of the electrolytes as shown in Figure 4-6a.

Equation (4-3) describes the rate constant of the MHC model  $(k_{red/ox}^{MHC})$ where Z is the pre-exponential factor accounting for the electronic coupling and the electronic density of states of the electrode, x is the energy, e is the elementary charge, and  $k_{\rm B}$  is the Boltzmann constant.<sup>[24]</sup>

$$k_{red/ox}^{MHC}(\eta) = Z \int_{-\infty}^{\infty} \exp\left(-\frac{\left(x - \lambda \pm e(E - E^0)\right)^2}{4\lambda k_B T}\right) \frac{1}{1 + \exp\left(x/k_B T\right)} \, dx \quad (4-3)$$

Since Z for Br<sub>2</sub> reduction in the polybromide is unknown, the current-overpotential equation for the MHC model, Equation (4-4), was derived, where  $\eta$  is the overpotential. The details for the derivation are shown in **4.7. Appendix**. Equation (4-4) normalizes the current to  $i_0$ , so it can be used without knowing the real surface area of the electrode. It is worth noting that  $\lambda$  is the only parameter determining the relationship between  $\eta$  and  $i/i_0$  according to Equation (4-4).

$$i/i_{0} = \frac{\int_{-\infty}^{\infty} \exp\left(-\frac{(x-\lambda-e\eta)^{2}}{4\lambda k_{B}T}\right)\frac{1}{1+\exp\left(x/k_{B}T\right)} dx}{\int_{-\infty}^{\infty} \exp\left(-\frac{(x-\lambda)^{2}}{4\lambda k_{B}T}\right)\frac{1}{1+\exp\left(x/k_{B}T\right)} dx}$$

$$-\frac{\int_{-\infty}^{\infty} \exp\left(-\frac{(x-\lambda+e\eta)^{2}}{4\lambda k_{B}T}\right)\frac{1}{1+\exp\left(x/k_{B}T\right)} dx}{\int_{-\infty}^{\infty} \exp\left(-\frac{(x-\lambda)^{2}}{4\lambda k_{B}T}\right)\frac{1}{1+\exp\left(x/k_{B}T\right)} dx}$$
(4-4)

 $\lambda$  for Br<sub>2</sub> reduction in MEPBr<sub>2n+1</sub> on the Pt surface were extracted from the cathodic forward scan of voltammograms by fitting the  $i/i_0$  vs.  $\eta$  data to Equation (4-4).  $i_0$  was achieved by the linear fit of the data at low overpotentials to Equation (4-5) as shown in **Figure 4-6b**. In Equation (4-5), *F* is the Faraday constant, and *R* is the gas constant. All the kinetics models, the BV model and the MHC model, converge to Equation (4-5) at low overpotentials.

$$i = -i_0 F\eta/RT \tag{4-5}$$

**Figure 4-6c** shows that the cathodic voltammogram in MEPBr<sub>2n+1</sub> at Pt was wellfitted to the MHC model with  $\lambda = 200$  meV. The average value for  $\lambda$  obtained on a Pt surface of 100 µm x 100 µm area with a hopping distance of 25 µm using the 570 nm diameter SECCM tip was 197 ± 4 meV (N = 24). The first landing data was not considered because its  $i_0$  is an outlier with twice the value with respect to the subsequently measured values.  $\lambda$  at the same Pt surface measured with the 160 nm diameter tip was  $198 \pm 5 \text{ meV} (N = 54)$ . These values agree well with the previously measured values ( $196 \pm 21 \text{ meV}$ ) investigated at a 10 µm diameter Pt UME in MEPBr<sub>2n+1</sub>, as discussed in Chapter 3. The lower standard deviation of the SECCM measurements compared to the UME system can be attributed to the highly-reproducible experimentation with high statistical validity offered by SECCM. This implies that the meniscus cell of the polybromide RT-IL droplet hanging at the end of the SECCM tip remains stable during multiple contacts with the electrode surface. Moreover, SECCM took advantage of the easy access of a new electrode surface for every experiment, minimizing the effects of surface corrosion on the measurement.



Figure 4-7. Scan rate effects on the measured  $\lambda$  value in MEPBr<sub>2n+1</sub>. (a) Scan rate dependence of CVs for Br<sub>2</sub> reduction in MEPBr<sub>2n+1</sub> on the Pt surface. The SECCM tip diameter was 570 nm. (b–c) Scan rate dependent (b)  $i_0$  and (c)  $\lambda$ . The number of the data points for averaging was 24.

Interestingly, the MEPBr<sub>2n+1</sub> voltammogram depends on its scan rate as shown in **Figure 4-7a**. This cannot be attributed to charging current effects because the charging current of MEPBr<sub>2n+1</sub> was negligible compared to the Faraday current. The electron transfer kinetics for Br<sub>2</sub> reduction as well as the mass transport are fast to amplify the Faraday current.<sup>[97]</sup> With the lower scan rate,  $i_0$  increased while  $\lambda$  2 set<u>s</u> to the set to th the relaxation time of the EDL in trioctylmethylammonium in the EDL caused by the strong short-range Coulomb interactions among ions.<sup>[133]</sup>

# 4.4.3. Reorganization Energy for Br<sub>2</sub> Reduction in MEPBr<sub>2n+1</sub> Subject to the Elemental Composition of the Pt-Pd-Ru-Ir-Ag HEA

To identify the effects of elemental compositions on the electrocatalysis in RT-ILs, the reorganization energies in MEPBr<sub>2n+1</sub> at different MAs, i.e. different compositions within the Pt-Pd-Ru-Ir-Ag HEA-ML, see Table 1, were explored. Scan hopping mode (10 µm x 10 µm area, 5 µm hopping distance) of SECCM using an 80 nm diameter tip filled with MEPBr<sub>2n+1</sub> was performed at seven MAs (MA1 – MA7) distributed across the HEA-ML (**Figure 4-8**). The derived reorganization energies at the seven MAs are summarized in **Table 4-1** and **Figure 4-9**. The  $\lambda$  values determined on the HEA-ML were higher than that of the Pt film. MA7 which has the highest Pt-content exhibited the smallest  $\lambda$  value among the seven MAs. This implies that Pt can effectively reduce the activation barrier for Br<sub>2</sub> reduction by alleviating the free energy required for structural changes accompanied by the



**Figure 4-8.** Atomic % of (a) Ir, (b) Pd, (c) Ru, (d) Pt, and (e) Ag, and (f) estimated WF for each measurement area (MA) in the HEA-ML. The estimated WF for each MA was calculated from the atomic % of each element. Black squares in (f) show the locations of the seven MAs where  $\lambda$  in MEPBr<sub>2n+1</sub> was measured.

**Table 4-1.** Elemental composition ratio (atomic %), the corresponding composition-weighted average work function (Estimated WF), and the  $\lambda$  for Br<sub>2</sub> reduction in MEPBr<sub>2n+1</sub> of the seven measurement areas (MA) of the HEA-ML.

Electrode	Ru	Pd	Ag	Ir	Pt	Estimated WF /eV	$\lambda$ / meV
MA 1	7.9	61.8	1.0	10.4	18.9	5.19	$295 \pm 5 \ (N=9)$
MA 2	10.6	56.2	0.8	12.8	19.6	5.19	$289 \pm 9 \ (N = 9)$
MA 3	17.6	45.7	0.8	15.4	20.5	5.18	$271 \pm 10 \ (N = 9)$
MA 4	22.6	39.7	1.1	17.3	19.3	5.15	$285 \pm 12 (N = 9)$
MA 5	26.8	35.1	1.6	18.7	17.9	5.13	$301 \pm 13 \ (N = 9)$
MA 6	17.2	45.2	0.0	25.1	12.4	5.15	$298 \pm 8 \ (N = 9)$
MA 7	15.2	40.4	1.4	9.9	33.1	5.25	$223 \pm 5 \ (N = 9)$



**Figure 4-9.**  $\lambda$  for Br<sub>2</sub> reduction in MEPBr<sub>2n+1</sub> at the seven MAs of the HEA-ML and polycrystalline Pt measured by SECCM.

electron transfer.

<u>.</u> (\*\*\*\*



Figure 4-10. The effects of electrode work function on  $\lambda$  for Br<sub>2</sub> reduction in MEPBr<sub>2n+1</sub>. (a) The correlation between the estimated WF and the  $\lambda$  on the seven MAs of the HEA-ML. (b) Schematic of the surface-charge dependent EDL structure in MEPBr<sub>2n+1</sub> and corresponding solvation structure.

eV (Pd), 5.3 eV (Ir), 4.7 eV (Ru), and 4.3 eV (Ag), respectively.<sup>[69]</sup> Intriguingly, a negative correlation between the  $\lambda$  and the estimated WF is observed as shown in **Figure 4-10a**. MA1 and MA2 in the HEA-ML which have high Pd contents slightly deviate from the trend. The WF is the key parameter determining the PZC of electrodes.<sup>[163]</sup> A direct linear relationship between the WF and the PZC with a slope of unity has been reported.<sup>[11]</sup> Therefore, **Figure 4-10a** suggests a negative correlation between  $\lambda$  and PZC of the HEA-ML in accordance with the surface charge-dependence of the net dielectric constant of the solvating medium in the IHP, which was proposed in our previous work.<sup>[151]</sup> As demonstrated in **Figure 4-10b**, electrodes with more negative PZC have more positive surface charges at the potential where Br<sub>2</sub> reduction occurs, and the ionic composition of the IHP in the RT-IL strongly depends on the electrode surface charges.<sup>[90]</sup> The positive charges on the electrode surface would cause the substitution of the MEP<sup>+</sup> in the IHP with Br<sup>-</sup> which is the anion having the highest negative charge density among anions in MEPBr<sub>2n+1</sub>. The redox-active species in RT-ILs are solvated by ions so that the altered ion

composition in the IHP can lead to a significant variation in the solvation energy. The outer-sphere reorganization energy in RT-ILs, which represents the reorganization of solvents, has been proposed to have a relationship of inverse proportion to the dielectric constant of the solvating ions.<sup>[121–123]</sup> MEP<sup>+</sup> (10–20) has higher polarizability than that of Br<sup>-</sup> (5.8).<sup>[137]</sup> Therefore, the increased  $\lambda$  at the electrode material with more negative PZC can be attributed to the less polarizable solvating ability of the IHP.

### 4.5. Conclusion

RT-IL electrocatalysts are promising given that they can offer a reaction environment that conventional solvents cannot provide. However, the interfacial structure-activity correlation has been less studied in RT-ILs compared to aqueous solutions. A complex EDL structure in RT-ILs where ion movements are strongly correlated to other ions and thus electrode surface charges, make it crucial to explicate the impacts of the EDL structure on electrochemistry in RT-ILs. In summary,  $\lambda$  for Br<sub>2</sub> reduction in MEPBr<sub>2n+1</sub> at polycrystalline Pt and an HEA-ML consisting of Pt, Pd, Ir, Ru, and Ag were explored using SECCM techniques. SECCM tips with nanoscale diameter are critical for obtaining electron transfer-limited voltammograms to extract  $\lambda$ . The voltammograms in MEPBr<sub>2n+1</sub> at Pt are well fitted to the currentoverpotential equation for the MHC model, yielding  $\lambda = 197 \pm 4$  meV. Taking advantage of SECCM, easy acquisition of many data points at a new electrode surface using a single sample electrode, the relationship between the  $\lambda$  in MEPBr<sub>2n+1</sub> and the elemental composition of electrodes was investigated using the HEA-ML. As a consequence, a negative correlation between  $\lambda$  and the estimated WF of the HEA-ML was observed. Attracting MEP<sup>+</sup> cations with higher polarizability rather than anions by negative charges at the electrode surface can reduce the solvation energy of the redox-active species in the IHP, leading to a smaller reorganization energy and facilitated electron transfer kinetics. This provides insight into the role of the surface charge-dependent IHP structure on electrochemical kinetics in RT-ILs. Furthermore, our work assures robust SECCM experimentation in RT-ILs as previously demonstrated in a few examples such as using 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm][BF4]),<sup>[164]</sup> 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIm][PF6]),<sup>[165]</sup> or 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide.<sup>[166]</sup>

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# 4.7. Appendix: Derivation of the current-overpotential equation for the MHC model

Electron-transfer rate-limited reaction assumes that the amount of electron transfer reactions is negligible with respect to any changes in the bulk concentrations of redox species ( $C_R^*$  and  $C_0^*$ ), thus their surface concentrations can be considered constant during electrochemical measurements. Then, the current can be expressed as follows (Equation (4-6)):

$$\frac{i}{nFA} = k_{ox}C_R^* - k_{red}C_O^* \tag{4-6}$$

Here, *i* is the current, *n* is the number of electrons per one reaction, *F* is the Faraday constant, *A* is the electrode surface area,  $k_{ox}$  is the oxidation rate constant, and  $k_{red}$  is the reduction rate constant. However, *Z* for Br<sub>2</sub> reduction in the polybromide and *A* are unknown, so the current-overpotential equation for the MHC model was derived. The definition of  $i_0$  is as follows:

$$\frac{i_0}{nFA} = k_{ox,\eta=0} C_R^* = k_{red, \eta=0} C_0^*$$
(4-7)

Dividing Equation (4-6) by Equation (4-7) yields Equation (4-8).

$$\frac{i}{i_0} = \frac{k_{ox}}{k_{ox,\eta=0}} - \frac{k_{red}}{k_{red, \eta=0}}$$
(4-8)

Assuming that  $E_{eq}$  equals  $E_0$ , substituting Equation (4-3) to Equation (4-8) yields the current-overpotential equation for the MHC model, Equation (4-4).

### **Chapter 5. Summary and Perspectives**

### 5.1. Summary

To meet the continuous but challenging demand for fundamental studies explaining electrocatalytic activities concerning the interfacial EDL structure, this thesis proposes methodologies evaluating the PZC and the reorganization energy within the EDL. Firstly, as presented in Chapter 2, SECCM allowed investigation of the local PZC on surfaces of complex material electrode, HEA, as well as single element electrodes like Pt and Au. The Pt-Pd-Ru-Ir-Ag HEA-ML with a content distribution of each element in different directions offered various PZC with a range from -0.23V to 0.39 V vs Ag/AgCl. This serves as a good model system to explore the influence of surface charge on electrocatalysis. Secondly, the reorganization energy for  $Br_2$ reduction in MEPBr<sub>2n+1</sub> ionic liquid was evaluated in Chapter 3. and Chapter 4. The electron transfer kinetics limited voltammogram for Br<sub>2</sub> reduction in the MEPBr<sub>2n+1</sub> with the surprisingly high diffusion coefficients of Br<sub>2</sub> and Br<sup>-</sup> was the key strategy to fit the voltammogram to the MHC model and subsequently obtain the reorganization energy. Ultramicroelectrode with spherical diffusion was first introduced to boost the mass transport of species in Chapter 3. In Chapter 4, enhanced mass transport was achieved through the use of the SECCM with nanopipettes. This enabled the investigation of the reorganization energy on the HEA surfaces which are challenging to prepare in the form of ultramicroelectrodes.

These methodologies allowed explicating the close relationship between electrode surface charges and the electrocatalytic activities, as exemplified in the HER in the acidic aqueous electrolyte and Br<sub>2</sub> reduction in the polybromide ionic liquids. As presented in Chapter 2. the HER in the perchloric acid solution on the HEA electrodes facilitated under the stronger negative electric field. Numerical modeling of the EDL structure with SECCM geometries revealed that the accumulated H<sup>+</sup> in the IHP to compensate the negative charges on electrode surfaces led to the HER current density dependent on the PZC. This preconcentration effect will become significant in confined spaces such as mesoporous and nanoporous electrocatalysts owing to their enlarged surface area-to-volume ratio.<sup>[22]</sup> Furthermore, the PZC of the HEA had a linear relationship with its elemental compositionweighted work function. This work provides the elemental composition designing principle of HEA to achieve high HER activities. On the other hand, the experimental results in Chapter 3. and Chapter 4. indicated the polarizability switch within the IHP according to the electrode surface charges, consequently influencing the electron transfer kinetics. This ion switch model was corroborated in TiO<sub>2</sub>@Pt (Chapter 3.) and the HEA consisting of Pt, Pd, Ir, Ru and Ag (Chapter 4).

### 5.2. Perspectives

EDL engineering, which controls the electrocatalytic activities by modulating the interfacial field strength and the solvation structure, is emerging as a promising electrocatalyst designing principle to complement the previous Sabatier principle. Interfacial electric field can regulate the electrocatalytic activities<sup>[18]</sup> and product selectivity.<sup>[167,168]</sup> Even spectator cations have influence on the product selectivity of complex multistep reactions,<sup>[40,169]</sup> and the binding strength of intermediates.<sup>[170]</sup> This thesis broadens applications of the EDL engineering to the acidic HER in HEA electrocatalysts and the electrocatalysis in the polybromide RT-IL. It is pointed out that the PZC of electrodes and the resulting compositional changes in the EDL can be important in controlling the electrocatalytic behaviors in both aqueous solutions and ionic liquids. The PZC of an electrode is primarily determined by its work function as demonstrated in Chapter 2. and Chapter 4. However, single element materials with similar work functions can have different PZC values as shown in the work of Trasatti,<sup>[1]</sup> which implies the possibility that there may be additional factors to control the EDL structure. The interfacial water orientation and the electronegativity of the electrode have been proposed as potential factors contributing to this phenomenon,<sup>[1,63]</sup> but it requires future studies to establish a clear conclusion. A HEA-ML consisting of various elements, e.g. noble metals and transition metals, can be a model system to study the relationship between the work function and the PZC. Applying the newly suggested methods for local PZC and the reorganization energy to various electrolytes will reveal innovative EDL engineering principles and open up new strategies for the electrocatalyst design.

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### 국문 초록

불균일 전자전달 반응이 일어나는 전국-전해질 계면 구조의 반응 환경을 이해하는 것은 효율적인 전기촉매 설계를 위해 중요하다. 특히 전국 표면에서 수~수십 nm 거리 공간에는 약 10<sup>9</sup> V/m 크기의 전기장이 걸려있는 전기이중층이 존재한다. 전기이중층의 강한 전기장은 용매의 분국을 유도하고 용매 배열 구조를 바꾸어 불균일 전자전달 속도상수 자체를 바꿀 수 있을 뿐 아니라, 전하를 띤 반응종과 생성물의 물질전달에도 영향을 줄 수 있다. 그러나 계면의 신호는 공간 크기가 큰 벌크 용액의 신호에 비해 약하며, 벌크 신호와 섞여 나오기 쉽다는 근본적인 실험적 한계로 벌크와는 다른 전기이중층 내부의 고유한 전자전달 반응 환경에 대한 연구는 더딘 상황이다.

본 논문에서는 산성 수용액에서의 수소 발생 반응과 이온성 액체 내 브로민 환원 반응을 예시로 전기이중층 구조가 전극 재료에 따른 전기촉매 활성 경향성을 기술하는데 중요한 변수임을 제시한다. 이는 반응 중간체의 흡착에너지가 전기촉매 반응성에 가장 중요하다는 사바티에 원리에만 크게 의존해왔던 전기촉매 설계 원리를 보완해준다. 1장에서는 전통적인 전기촉매 지시자 이론인 사바티에 원리를 설명하고, 사바티에 원리의 한계점들을 소개한다. 2장에서는 주사 전기화학 셀 현미경 기술과 고엔트로피 합금 재료 라이브러리 전극을 이용하여 합금의 원소 조성에 따른 전극의 영전하전위와 수소 발생 반응성을 스크리닝함으로써, 고엔트로피 합금의 수소 발생 전류가 전극의

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1 <list-item>[ \\d 치지 전자전달 속도론 이론을 기반으로 폴리브로마이드 이온성 액체 내 브로민 환원 반응의 재배열 에너지를 측정할 수 있는 방법론을 개발하였다. 백금 전극 표면에 양전하를 띠는 티타늄 옥사이드를 **)**</sup></sup> <table-cell></sup></sup> <form> 4/ eeeneeeneieiiieiiieeiiiiii-e}i-에너지를 측정하는 방법론을 보고하였다. 이 방법은 마이크로 전극으로 <caption>h<image>h th \\ 에너지 측정 결과는 3장에서 제안한 전극 표면 전하에 따른 내부 헬름홀츠 층의 용매화 구조 변화 모델을 뒷받침한다.

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