

# Adsorption and friction of Mussel Adhesive Protein (MAP) films under polarization

G.X. Xie<sup>1,2,\*</sup>, F. Zhang<sup>1</sup>, J.S. Pan<sup>1</sup>

<sup>1</sup>) Division of Surface and Corrosion Science, Department of Chemistry, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden.

<sup>2</sup>) State Key Laboratory of Tribology, Tsinghua University, Beijing 100084, China.

\*Corresponding e-mail: xie-gx@163.com

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**ABSTRACT** – Mussel Adhesive Protein (MAP) is an adhesive protein derived from blue mussel byssus, and has promising applications for a variety of functional coatings. In this work, different analytical techniques including cyclic voltammetry, chronocoulometry experiments, and microtribometer have been used to investigate the interfacial structures and the frictional properties of MAP film on the platinum (Pt) substrate under polarization. MAP adsorption could change electrostatically after polarization. The friction of adsorbed MAP film can be tuned effectively in a suitable potential range, which is promising for future active control over the adsorption and friction of MAP films.

## 1. INTRODUCTION

Mussel Adhesive Protein (MAP), a protein derived from blue mussel byssus, has found use in functional coatings, for example, biomedical glue and corrosion protective coating [1-3], and it has potential applications in ocean systems. In order to make these coatings more efficiently in these applications, some important scientific problems ahead still need to solve. For example, how to make the MAP films as dense and also stable as possible? Can we actively control the MAP film to function effectively or lose function? How about the durability of the films under liquid shear? On the basis of the molecular structure of the MAP molecule, two alternative treatments could be used to enhance the film compactness: 1) Adsorption amount can be changed by controlling the electrostatic interaction between charged groups on the molecule; 2) Film density can be increased by inducing dopa oxidation and cross-linking. Theoretically, both treatments can be realized by the change of PH value or electrochemical polarization. Previous work conducted by Krivosheeva, et al demonstrated the feasibility of using PH value change to control the adsorption amount of MAP on substrates which was mainly driven by electrostatic interaction [1]. Yu et al. [2] showed that change of the MAP chemical structure, i.e. oxidation, could be induced by raising the solution PH value, resulting in the decrease of adhesion of MAP. However, the reversibility was shown to be not very good. For polarization control over MAP adsorption properties and corresponding performances, very few works has been reported till now. In this work, we intend to show some

results of the adsorption and frictional behaviors of MAP films under polarization to get more information about the relationship between the delicate interfacial properties of MAP film after being polarized and adsorption/friction.

## 2. METHODOLOGY

Different analytical techniques including CV, chronocoulometry experiment, electrochemically controlled quartz crystal microbalance (E-QCM), electrochemically controlled atomic force microscope (E-AFM) and microtribometer were used in the present work. CV was used to find the suitable tuning electrochemical window; chronocoulometry experiments and E-QCM were used to evaluate the adsorption and interfacial information of MAP films; E-AFM was used to characterize the morphology of the MAP film; Microtribometer was used to test the frictional properties under polarization, as schematically shown in Figure 1. The solutions used in this work were citric acid (CA) with and without MAP molecules. The working electrode was a polished platinum (Pt) foil.

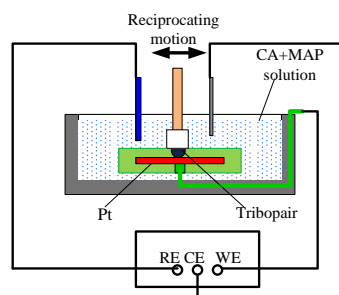


Figure 1 Schematic of microtribometer under polarization.

## 3. RESULTS AND DISCUSSION

Figure 2 is the typical CV results of 0.1 mg/mL MAP in the CA solution at different scanning rates. Generally, three regions can be divided in the graph: The left part region where two peaks in both the anodic and cathodic scans can be observed. These peaks are associated with hydrogen-adsorption sites. The middle part is the electric double layer part; The right part is the oxidation region of the Pt surface and the MAP film. As the scanning rate increases, the peak currents increase correspondingly, and the peak potentials shift slightly.

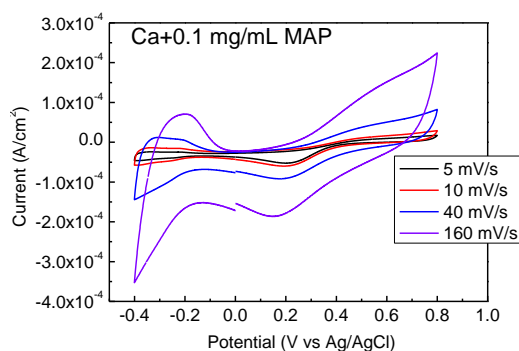


Figure 2 CV curves of the MAP solution (0.1 mg/mL) at different scanning rates.

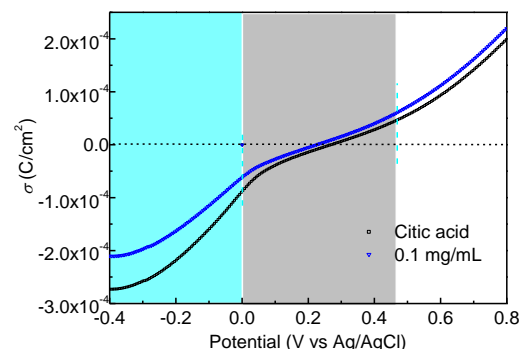


Figure 3 Calculated absolute charge density at Pt electrode surface from the measured difference of the charge densities and the point of zero charge (pzc) based on the chronocoulometry experiment.

Figure 3 is the calculated absolute charge on the Pt surface. Theoretically, the change in the potential of zero charge ( $\Delta E_{pzc}$ ) due to the displacement of surface water by the adsorbed MAP film can be written as [4]:

$$\Delta E_{pzc} = \Gamma(\mu_{org} - n\mu_w) / \epsilon \quad (1)$$

Where  $\mu_w$  and  $\mu_{org}$  are the average components of the permanent dipole moment of the water and organic molecules in the direction normal to the surface, respectively.  $n$  is the displaced water molecule number from the Pt surface by one adsorbed MAP molecule, which  $\Gamma$  is the maximum surface concentration of the MAP molecules, and  $\epsilon$  is the permittivity of the inner layer. When the potential  $< 0$ ,  $\mu_w > 0$ ,  $\mu_{org}$  must be negative, suggesting more oxygen atoms on MAP molecules facing the Pt substrate. When the potential  $> 0$ ,  $\mu_w < 0$ , if  $\Delta E_{pzc}$  is larger (in magnitude), it means more oxygen atoms face the Pt substrate, and the part with positive charges faces the solution.

Figure 4 shows the change of the coefficients of friction (CoFs) over time at different switching potential ranges in the MAP solution (0.01 mg/mL). It can be seen that at cathodic potentials, the CoFs are relatively low and also close both at -0.4 V and -0.8 V, while they increase dramatically when the potential is switched towards the anodic direction. As compared with 1.2 V and 1.8 V, the CoF is relatively lower at 0.8 V, however, the CoFs at the two larger anodic potentials are also very close. It may be due to the influence of oxygen release around the contact region between the tribopairs.

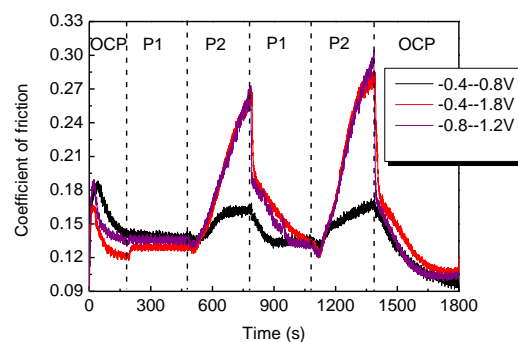


Figure 4 Variations of CoF over time in different switch potential ranges in the MAP (0.01 mg/mL) solution. P1 indicates the low potential, and P2 the high potential.

#### 4. CONCLUSIONS

The present work attempts to demonstrate the feasibility of changing the MAP adsorption properties and corresponding frictional performance with polarization controls by using the combination of different analytical techniques. Some electrochemistry and friction results are shown here, and more data will be shown at the conference. In generally, our results indicate MAP adsorption and friction could change obviously after polarization provided that a suitable potential range is used, which is of scientific importance to better understand the interfacial properties of this specific protein film and also of significance for its future practical application.

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