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# Catalytic hydrogen evolution by polyaminoacids using mercury electrode

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## Abstract

It was shown that using constant current chronopotentiometric stripping (CPS) peptides and proteins at nanomolar concentrations produce protein structure–sensitive peak H at mercury electrodes. This peak is due to the catalytic hydrogen evolution reaction (HER). Polyamino acids can be considered as an intermediate model system between peptides and macromolecular proteins. Here we used polyamino acids (poly(aa)) such as polylysine (polyLys) and polyarginine (polyArg) and cyclic voltammetry or CPS in combination with hanging mercury drop electrode to explore how different amino acid residues in proteins contribute to the catalytic HER.

**Keywords:** constant current chronopotentiometry, mercury electrodes, polyaminoacids, electrocatalysis

## Introduction

First paper on electrochemistry of proteins was published by Heyrovský and Babička in 1930 describing the d.c. polarographic "presodium wave". Soon it was shown that cysteine–containing proteins produce well–developed Brdička's double wave (Brdicka's catalytic response, BCR) (Brdicka, 1933). Both the presodium wave and BCR were shown to be due to the catalytic hydrogen evolution. Recently, we have shown that using CPS with hanging mercury drop electrode (HMDE), peptides and proteins yield at negative potentials a well developed peak (peak H) in buffered solutions, regardless of the presence or absence of cobalt (Palecek and Ostatna, 2007; Tomschik et al., 1998). Here we show that and polyArg produced CPS peak H at low bulk concentrations at highly negative potentials due to HER.

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## Materials and methods

Polylysine, MW = 4000 – 15000 (poly-L-Lys 4-15), polylysine MW = 30000 – 70000 (poly-L-Lys 30-70), and polyarginine MW = 5000 – 15000 (poly–L–Arg 5-15) were purchased from Sigma–Aldrich. In all adsorptive stripping experiments, the analyte was adsorbed on the hanging mercury drop electrode (HMDE) surface from the stirred solution containing poly(aa) solution in the background electrolyte at a given accumulation potential ($E_A$), during the chosen accumulation time ($t_A$); then chronopotentiograms or voltammograms were recorded.

## Results and Discussion

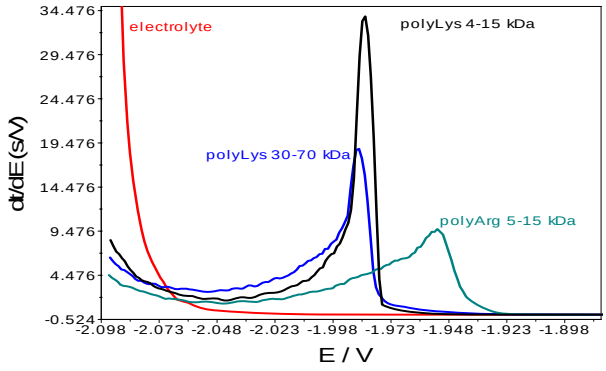


Figure 1: Adsorptive stripping CPS~~A~~ peak H of 0.5 μM poly–L–Lys 30–70, 0.5 μM poly–L–Lys 4–15, and 0.5 μM poly–L–Arg 5–15. Background electrolyte: 0.05 M McIlvaine buffer, pH 6. $I_{str}$ = − 30 μA, $t_A$ = 60 s, $E_A = E_i$ = − 0.1 V, $E_f$ = − 2.1 V, 23.7 °C. Poly(aa) concentrations are related to their monomer content.

Our results show that lysine or arginine residues in a polypeptide chain are sufficient to induce catalytic HER at the HMDE. We found that at pH 6 both polylysine and polyarginine produced comparable peaks H under the given conditions.

## Conclusion

In recent years catalytic HER of proteins measured by CPS at HMDE and amalgam electrodes appeared as a new tool in protein analysis (Doneux et al. Palecek and Ostatna 2007). High sensitivity

and low volume requirements (femto– and attomoles of proteins can be analyzed) as well as simple and inexpensive instrumentation made this method attractive for applications in proteomics and biomedicine. This work represents an attempt to apply poly(aa)'s to contribute to elucidation of catalysis of HER by proteins.

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