Cyclic Voltammetry

Chemicals and Instruments

N_2-purged solution of 0.5 M H_2SO_4
N_2-purged 2 mM solution of *N,N,N',N'*-tetramethyl-*p*-phenylene diamine in 0.5 M H_2SO_4
Potentiostat
2 Pt electrodes
Ag/AgCl/KCl(sat'd) reference electrode
Electrochemical cell or 3-necked flask

Electrode Reactions with Coupled Homogeneous Chemical Reactions (B&F Chapters 6 and 12, also Nicholson & Shain)

Task

Use cyclic voltammetry to derive a reaction pathway for the electrooxidation of *N,N,N',N'*-tetramethyl-*p*-phenylene diamine.

Fundamentals

In homework set 3 (B&F question 6.9), we analyzed cyclic voltammetry data for azotoluene. In this laboratory exercise we will study cyclic voltammetry for *N,N,N',N'*-tetramethyl-*p*-phenylene diamine and apply the analysis techniques we have learned using our experimental data. Figure 1 shows the structure of the molecule and examples of typical cyclic voltammograms with the upper potential limit varied.

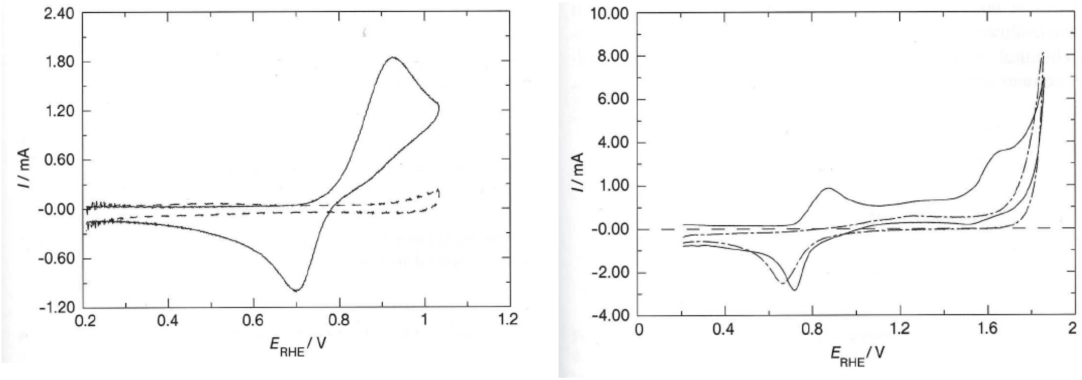

Figure 1. (left) Structure of *N,N,N',N'*-tetramethyl-*p*-phenylene diamine. (center and right) Cyclic voltammograms of a 2 mM solution of *N,N,N',N'*-tetramethyl-*p*-phenylene diamine in 0.5 M H_2SO_4 (solid curves) with CVs for the electrolyte solution shown with dashed lines. The scan rate was 100 mV/s for both.

Procedure

Use a Pt working electrode, Pt counter electrode, a Ag/AgCl/KCl (sat'd) reference electrode and a potentiostat to record cyclic voltammograms for the solution of *N,N,N',N'*-tetramethyl-*p*-phenylene diamine at varied scan rates and for the two scan windows shown in the Figure 1.

Try to get your range of scan rates to cover at least a factor of 10, as Nicholson & Shain and Prof. Bocarsly tell us to do. Since the maximum scan window looks to be 0–1.6 V versus Ag/AgCl, a complete scan at 20 mV/s will require less than 3 minutes, so that seems like a reasonable lower limit for the scan rate (provided data also looks good at 200 mV/s).

Collect data using at least 5 scan rates, the more data you collect the better you will be able to fit the current functions.

Work-Up and Questions

1) Plot your cyclic voltammetry data for each scan rate, including overlays for the baseline scans. To do this neatly you may need a separate plot for each scan-window/scan-rate combination.
2) Use your data to make a table including i_{pc}, i_{pa}, E_{pc}, E_{pa}, and $E_{p/2}$(as applicable), similar to the table that accompanied B&F question 6.9.
3) From the peak ratios and dependence of peak position on scan rate, comment on whether each wave appears reversible or irreversible.
4) Use appropriate plots and fits to analyze the data. Assume n=1. For each reversible wave, determine a diffusion coefficient. For each irreversible wave, determine α, and a diffusion coefficient.
5) For each wave, which mechanism from Nicholson & Shain best fits the data?
6) Speculate as to a possible chemical mechanism for the observed behavior.

Adapted from Holze, R. *Experimental Electrochemistry A Laboratory Textbook*. Wiley-VCH, Darmstadt. 2009.