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## ACCEPTED MANUSCRIPT

## EFFECT OF SURFACE STRUCTURE OF PLATINUM SINGLE CRYSTAL ELECTRODES ON THE ELECTROCHEMICAL REDUCTION OF CO<sub>2</sub> IN METHANOL-WATER MIXTURES

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Abstract: The reduction of  $CO_2$  on platinum single crystal electrodes has been investigated in methanol/water mixtures. The reaction is sensitive to the crystallographic structure of the surface, with the (111) triangular arrangement of atoms being the most active site. Use of stepped surfaces revealed that long range order has little effect on the reaction rate. On the other hand, the (100) site is the less active. The combination of the results of a voltammetric study using different scan rate and the use of a hanging meniscus rotating disk electrode configuration with different rotation speeds suggests the reaction rate is limited by a chemical step at large overvoltages. The nature of this chemical step is uncertain but different possibilities are discussed. The Tafel slope suggests that the rate determining step is the first electron transfer at low overvoltages while at high overvoltages the rate of the first chemical step limits the rate of  $CO_2$  reduction.

Keywords: CO<sub>2</sub> reduction, platinum single crystal electrode, methanol water mixtures, cyclic voltammetry, hanging meniscus rotating disk electrode, FTIRRAS spectroscopy.

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