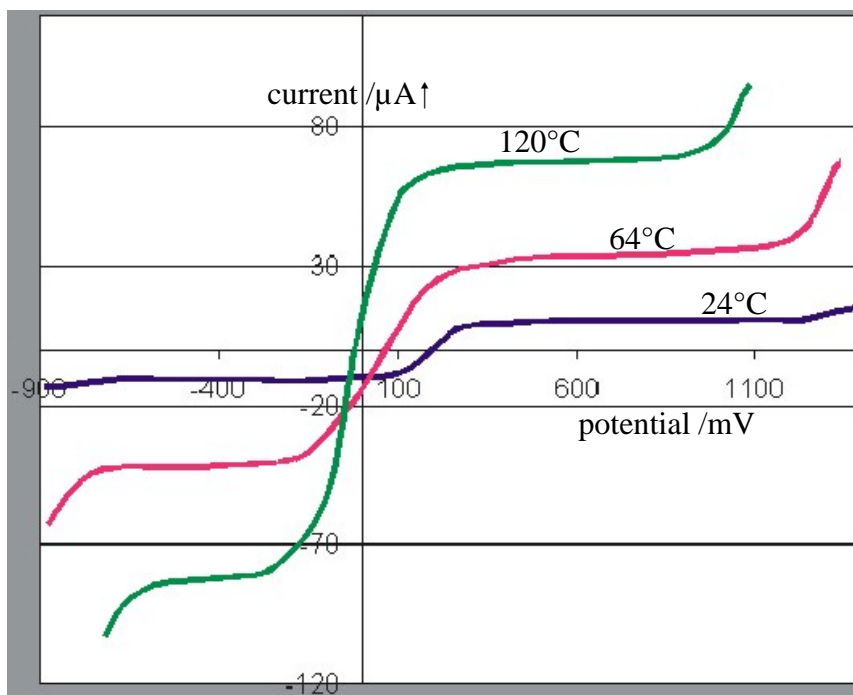


### In-situ Thermoelectrochemistry

Thermoelectrochemistry is an underdeveloped subject if compared with other combination techniques like spectroelectrochemistry. A modern approach is arising now, since in 1993 the direct heating of microwire electrodes has been invented by Gruendler et al. This was the first way to vary temperature as an independent variable in electrochemistry. Later comparative techniques (electrode heating by microwaves etc.) have been proposed.

Actual „hot-wire“ techniques allow to perform voltammetry in metastable, overheated water (at atmospheric pressure, without autoclaving), as shown below. The curves are composed of hundreds of single measuring points, each taken by fast electrode temperature rise followed by fast decay. Processes are fast enough to prevent formation of vapour bubbles. Temperature values far above the boiling point can be achieved in an open, non-pressurized system.

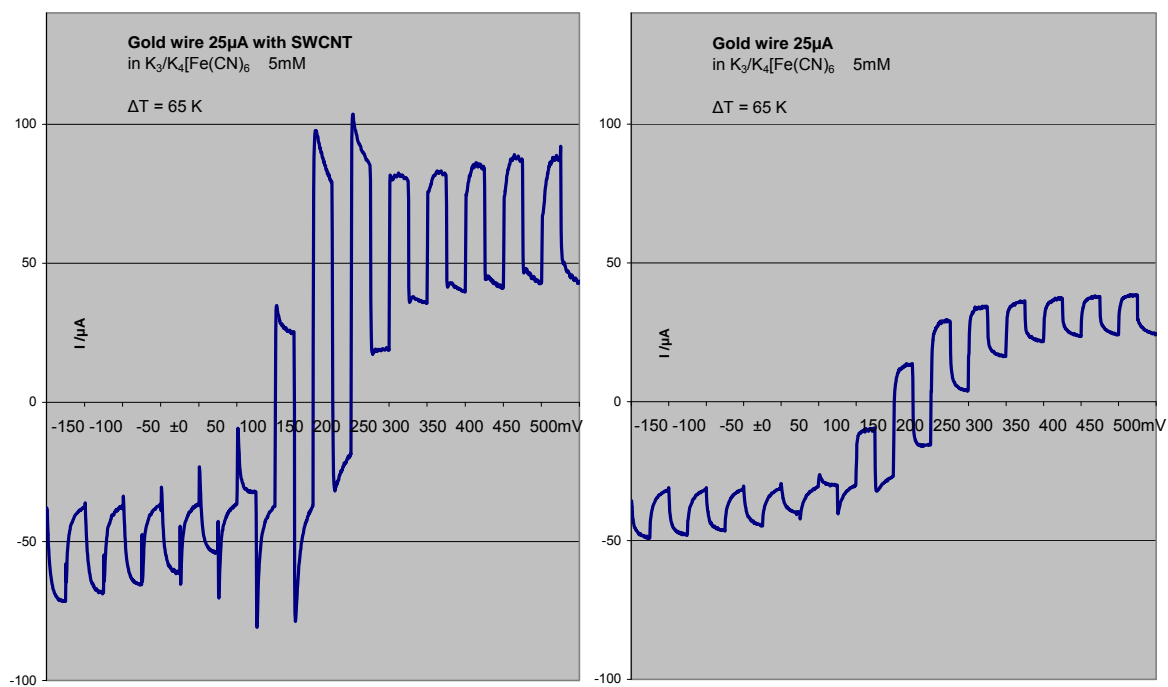


#### Temperature-pulse voltammograms (TPV).

Ferrocyanide/ferricyanide 5mM in 0.1M KCl. Heated Pt electrode, 25μm.

Theoretical interpretation of results in thermoelectrochemistry is assisted by „thermoelectrochemical spectra“ (see below). Kinetic as well as thermodynamic behaviour of heated electrodes is depicted. Under certain conditions, electrolytic current may reverse its sign just by temperature change. I.e. an electrode may act as an anode in hot and as a cathode in cold state, without changing the applied electrode potential.

In our department, heated thin wire microelectrodes are used to study the thermal behaviour of modern carbon structures. Successful preparation of a 25μm gold wire with a dense layer of single-wall carbon nanotubes allows to vary temperature extremely fast over a wide range in the course of electrochemical experiments.



**Thermoelectrochemical spectra.**

Gold wire electrodes (left: covered by SWCNT; right: bare). A potential staircase overlaid by a series of heat pulses, each generating a temperature jump of 65 K.