A Novel X-Ray Diffraction Technique for in-situ Observations of Cathode/Anode Reaction in Electrolytes

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Introduction

In-situ XRD can be used to analyze surface changes of electrodes and chemical structure of deposited layers during electrochemical measurements. Changes in the analysis result due to contact with air or degradation over time can be eliminated. Normally, the radiation source for these experiments need to have high intensity to make up the absorption of X-rays in the aqueous electrolyte. Therefore, synchrotron radiation sources are the standard.

The new cell design makes it possible to analyze thin film electrodes with a laboratory scale radiation source. It also solves common problems with bulk solution resistance or inhomogeneous current-density.

Deposition

The cell was tested with the well-known deposition reaction of Cu\textsubscript{2}O \cite{2,3} on Cu. In the galvanostatic mode with a cathodic polarization the growth of Cu\textsubscript{2}O on Cu was observed. After changing to the polarization the transformation of Cu into Cu\textsubscript{2}O was only seen when the Cu\textsubscript{2}O layer had reached a certain thickness.

\begin{figure}[h]
  \centering
  \includegraphics[width=\textwidth]{Fig1.png}
  \caption{Schematic view of the XRD in-situ cell (left) and 3D model (right). (1) CE, (2) RE, (3) solution inlet, (4) solution outlet, (5) solution chamber, (6) sputtered copper foil, (7) deposited copper oxide.}
  \label{fig:fig1}
\end{figure}

\begin{figure}[h]
  \centering
  \includegraphics[width=\textwidth]{Fig2.png}
  \caption{Photo of the measurement setup. The X-ray diffractometer Empyrean from PANalytical was used with a parallel plate mirror on the source side and a point detector.}
  \label{fig:fig2}
\end{figure}

\begin{figure}[h]
  \centering
  \includegraphics[width=\textwidth]{Fig3.png}
  \caption{Signal intensity for varying incident angles.}
  \label{fig:fig3}
\end{figure}

\begin{figure}[h]
  \centering
  \includegraphics[width=\textwidth]{Fig4.png}
  \caption{Galvanostatic cathodic deposition of Cu\textsubscript{2}O on Cu, left: Diffractogramms measured during deposition, right top: Intensity changes over time, right bottom: Potential over time.}
  \label{fig:fig4}
\end{figure}

\begin{figure}[h]
  \centering
  \includegraphics[width=\textwidth]{Fig5.png}
  \caption{Galvanostatic anodic deposition of Cu\textsubscript{2}O on Cu/Cu2O, left: Diffractogramms measured during deposition, right top: Intensity changes over time, right bottom: Potential over time.}
  \label{fig:fig5}
\end{figure}

Summary

- In-situ XRD setup usable with laboratory equipment– no synchrotron radiation source required
- Analysis method for thin films in the nanometer range (>50 nm)
- Wide WE material range (only two restrictions: material must be sputterable and conductive)
- No (or little) depletion of electrolyte because of big electrolyte volume
- Information about layers formed at the interface electrode/electrolyte

References:

\cite{1}

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