

## Stability of Fe Electrode in Alkaline Electrolyte

Shu Fen Tan,<sup>1,2</sup> Joseph S. Manser,<sup>3</sup> Maria Ronchi,<sup>3</sup> Sylvia Smullin,<sup>3</sup> Yet-Ming Chiang<sup>1,3</sup> and Frances M. Ross<sup>1</sup>

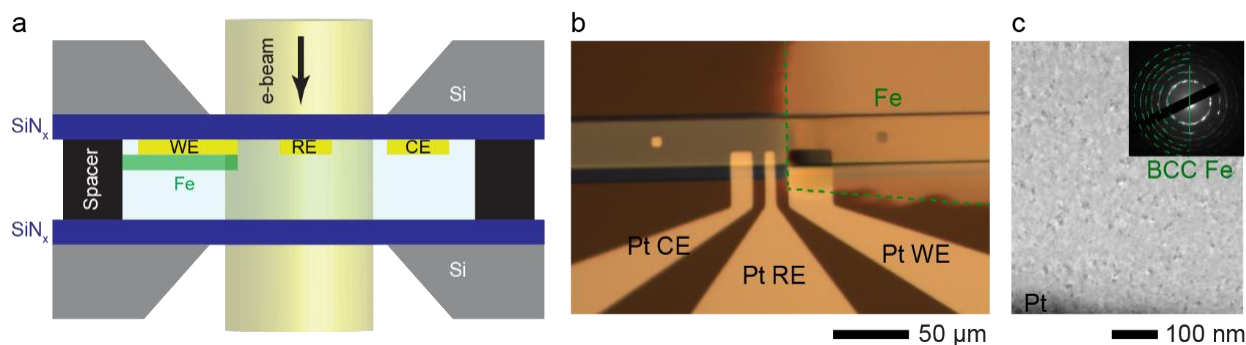
<sup>1</sup> Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States.

<sup>2</sup> School of Materials Science and Engineering, Nanyang Technological University, Singapore.

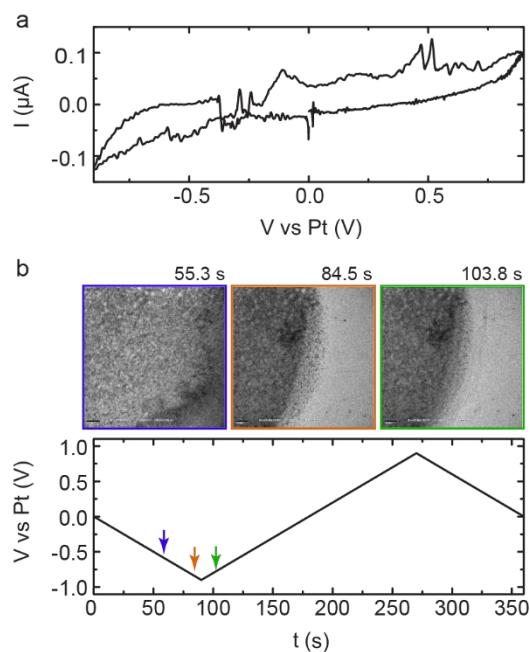
<sup>3</sup> Form Energy, Cambridge, MA, United States.

Non-precious metals such as Fe, Co, and Mn are potential candidate materials for electrodes owing to their low cost and high natural abundance. In particular, Fe-based materials have been explored as next generation electrode materials for energy storage and conversion applications ranging from batteries<sup>[1]</sup> to fuel cells<sup>[2]</sup> due to the lack of dendritic growth in alkaline electrolyte systems.<sup>[1, 3]</sup> However, a critical problem of Fe is its low stability in harsh conditions such as strong acidic or alkaline media during liquid-phase (electro)chemical reactions. Tremendous effort has been made on improving Fe electrode through additives<sup>[4]</sup> and electrode design,<sup>[5]</sup> yet the failure mechanisms of Fe electrodes, such as dissolution, passivation and self-discharge, are poorly understood. Further improving the performance of the Fe electrode requires a good understanding of Fe electrode stability under typical electrochemical conditions so as to understand the interplay of kinetic and thermodynamic phenomena such as initial electrode microstructure, electrolyte composition and cycling regime.

Here, we explore the possibility of using operando liquid cell electron microscopy with high spatial and temporal resolution as a direct probe to examine the stability of the Fe electrode in aqueous alkaline electrolyte under potential cycling conditions (Figure 1a). We used electron beam deposition through a shadow mask to pattern a BCC Fe thin film over the as-supplied Pt working electrode (Figure 1b-c). We then examined the stability of the electrode in terms of chemical, electrochemical and beam damage. Liquid cell TEM has predominantly been used in neutral or acidic conditions, thus we first assess the stability of the Fe electrode in alkaline electrolyte under electron beam irradiation with no bias. We further investigate the behavior of the Fe electrode in different alkaline electrolyte composition under cyclic voltammetry conditions (Figure 2a). We observe several microstructural changes including a thin layer of material deposition upon switching from reducing to oxidizing potential (Figure 2b). Our real-time imaging shows that the electrochemical processes on Fe electrode during potential cycling are intrinsically complex and fascinating and can be related to stability predictions from the Pourbaix diagram. Exploring the possibility of non-precious metals as electrode materials potentially opens up new opportunities for solving a range of problems relating to battery and electrocatalyst design.<sup>[6]</sup>



**Figure 1:** Fe electrode fabrication onto electrochemical liquid cell chip. (a) Schematic of electrochemical liquid cell experiment set-up. (b) Optical image shows the placement of as-deposited Fe thin film onto one of Pt electrodes on electrochemical liquid cell chip. (c) TEM image shows the as-deposited Fe thin film, diffraction pattern shown in inset confirms the initial Fe is BCC Fe.



**Figure 2:** Electrochemical stability of Fe electrode in alkaline electrolyte solution under cyclic voltammetry conditions. (a) CV cycle scanning from 0 to -0.9 V to +0.9 V and back to 0 V at 10 mV/s using the electrochemical liquid cell with geometry shown in Figure 1 and filled with 0.1 M KOH alkaline electrolyte. (b) Time-lapse TEM sequential images with the potential for each image (top panel) indicated by arrows shown in the applied potential versus time plot during the CV cycle (bottom panel).

## References

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