Abstract #2339, 224th ECS Meeting, © 2013 The Electrochemical Society

Silver Electrodeposition From Ionic Liquids: Coatings Morphology and Mass Transport Issues

S. Cinotti[1], L. Becucci[1], E. Banchelli[2], M. Innocenti[1,3,†], L. Luconi[2], L. Wang[3,4], A. Lavacchi[3,†,*]

[1] Department of Chemistry, University of Firenze, Via della Lastruccia, 3, 50019 Sesto Fiorentino (FI), Italy
[2] BLUCLAD s.r.l, via del Molinuzzo 8/G, 59100 Prato (PO), Italy
[3] ICCOM-CNR, via Madonna del Piano, 10, 50019 Sesto Fiorentino (FI), Italy
[4]CENMAT, University of Trieste, Via Valerio 2, 34127 Trieste, Italy

The paper focuses on the silver electrodeposition from a silver tetrafluoroborate solution in 1-butyl-3-methyltetrafluoroborate. In a previous study the dependence of the coating morphology on the temperature for the same system was investigated [1]. Here the main purpose is the understanding of the effect of the current density on the coating morphology.

Preliminary deposition experiments showed that the deposition limiting current densities in the investigated Ionic Liquid were much smaller than those commonly found in water base electrolytes. This holds both in the case of still and stirred solutions. We believe that the viscosity of the Ionic Liquids plays an essential role here. Hence hydrodynamic calculations on a simple model system for the understanding of the peculiarity of the mass transport in the Ionic Liquids were perfomed. The electrochemical deposition of silver in [BMIM][BF_4] was also studied by cyclic voltammetry using a gold electrode as a substrate to determine the diffusion coefficient of the silver ions by the Randles-Sevcik approach. A value of $7.62\ 10^{-7}$ $cm^2\ s^{-1}$ has been obtained, much lower than common values for water electrolytes (typically ranging around 10^{-5} $cm^2\ s^{-1}$) . The solvodynamic radius of silver has been estimated from the diffusion coefficient assuming the Stokes-Einstein relation. Calculation resulted in a value of 0.12 nm which is very close to the ionic radius of the silver ions in ionic compounds. We concluded that silver ions are not coordinated by the liquid.

5 µm thick and compact silver coatings have been obtained under galvanostatic conditions. The main experimental evidence has been the dramatic dependence of the grain size on the deposition current density (figure 1). We have found that higher current density produce coatings with lower grain size. Nevertheless in our experiments we couldn't operate with current densities exceeding 0.2 A dm^{-2}, even under vigorous stirring, since no compact coatings resulted under these conditions. In order to rationalize such findings we have performed both hydrodynamic calculations on model cells and measurements with the rotating disk electrode. We have found that the high viscosity of the [BMIM][BF_4] dramatically limits the mass transport even if strong convection is applied. Such an aspect have been scarcely considered so far but in the opinion of the authors it is crucial for a critical assessment of the potential impact of IL's in industrial galvanic processes.

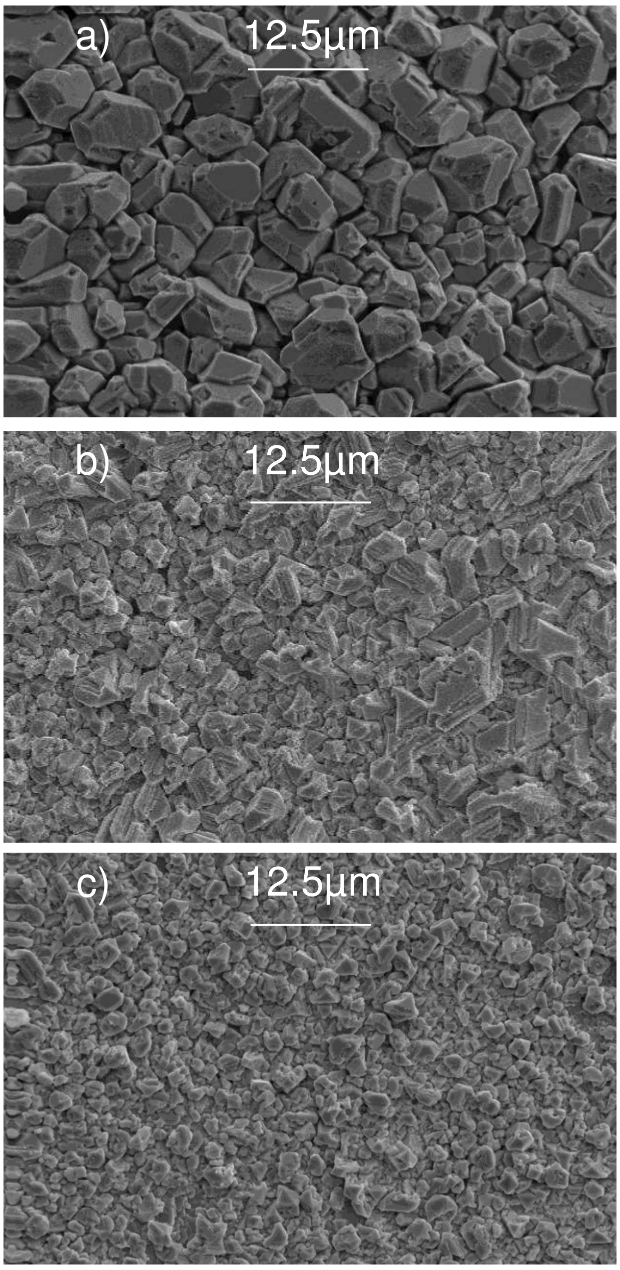

Figure 1: scanning electron micrographs of galvanostatic silver coatings obtained from a 0.1M [$AgBF_4$] solution in [BMIM[BF_4] at 0.05 (a) , 0.1 (b) and 0.2 A dm^{-2}(c).

References

R. Bomparola, S. Caporali, A. Lavacchi and U. Bardi Surface and Coatings Technology 201 (2007), 9485-9490.

[†] ECS active members
* Corresponding author