ChemComm

Supporting Information

An Air-Stable, Aluminium-Based Ionic Liquid Electrolyte for Energy Storage

Matthew Stalcup, Mia Blea, Elena Medina, Stephen J. Percival,* and Erik D. Spoerke**

Sandia National Laboratories, Albuquerque, New Mexico 87185, USA

*sperciv@sandia.gov Phone: +1 (505) 845-0207

**edspoer@sandia.gov Phone: +1 (505) 284-1932

Experimental Methods

All electrolytes were constructed on the benchtop without the use of an inert atmosphere. The chemicals were purchased commercially from various vendors. $AlCl_3$ (97% Fischer Scientific) and NaI (99.9%) were purchased from Millipore Sigma. The Ionic liquid EMIM[TFSI] (99.5%) was purchased from Solvionic. No further purification or drying of the chemicals were pursued. After the solids were added to the ionic liquid, they were gently heated and stirred at 30 °C until dissolved. Solutions were stored in scintillation vials until they were used.

Electrochemical experiments were all conducted using a Gamry Reference 600+ potentiostat. The electrochemical cell consisted of a glass cell (BASi) with a Teflon cap with holes for the electrodes. For all experiments a Pt wire and coil were used as the working and counter electrodes respectively. For cyclic voltammetry and the chronopotentiometry experiments, a 3 mm diameter Ni disk electrode (BASi) was used. Before any experimentation the electrode was polished with 1200 grit SiC sandpaper (Buehler) using a figure eight polishing motion. After experimentation, the electrode was rinsed using isopropyl alcohol followed by distilled water and cleaned with Kimwipes. The remaining electrolyte was transferred into scintillation vials and stored.

Electrolysis experiments for the purpose of imaging through SEM were conducted slightly differently. The Ni electrode we had previously used was too large to be used in the SEM so a Ni foil (99.99%, Alfa Aesar) was used. Additionally, Ni was chosen as a model substrate due to our ability to differentiate the deposited material from the substrate. The foil was masked with chemical resistant epoxy (Loctite EA 0151) and left to cure for at least 24 hours to ensure a well-defined electrode surface area. The resulting foil was then imaged, and the surface area was measured to ensure current density calculations were as accurate as possible. Those foils were then subjected to the same experimental setup and post processing mentioned above.

Raman experiments were conducted using a ThermoFisher Scientific DXR Smart Raman system with a 780 nm laser. To examine if the speciation of the electrolyte changed due to initial composition or as a function of electrochemical charge passed, we did a series of electrochemical experiments at various current densities 0.01, .01, 0.2, and 0.5 $mAcm^{-2}$ for 5 and then 15 minutes. Raman was always run after all the current densities for a given time were completed. The 15 min experiment had difficulties maintaining the current density for the entire duration most likely due to the 1 mL volumes of these solutions and the decreased mass transfer to the surface.

Scanning Electron Microscopy (SEM) images were captured on a FEI Verios 5 UC, using an accelerating voltage of 15 kV. Energy Dispersive X-ray spectroscopy (EDX) analysis was obtained using an EDAX Octane Elite Super with a 70 mm^2 Octane Elite silicon drift detector. Samples for SEM were fixed to stages using carbon tape and to limit the charging of the samples an additional piece of copper tape was then attached to each of the samples and then to the stage of the SEM to ensure proper connection.

Supplementary Figures

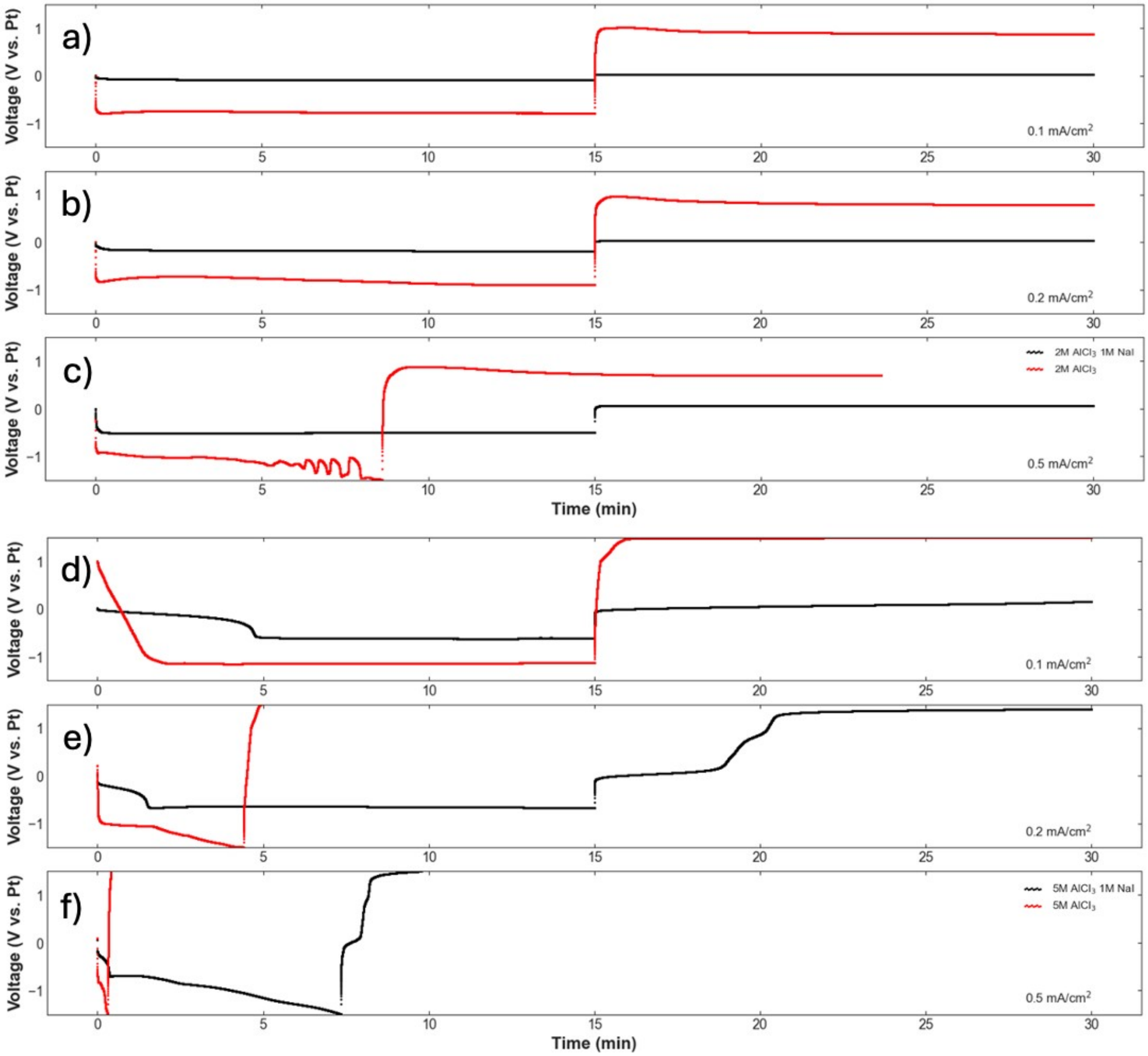

Figure S1. Constant current reduction and oxidation curves for EMIM/[TFSI] ionic liquid electrolytes containing 2M (a-c) and 5M (d-f) $AlCl_3$, with and without 1 M NaI. Current densities were varied from 0.1 to 0.5 mA/cm^2. Experiments were conducted on a 3 mm diameter Ni electrode with Pt coil counter and Pt wire reference.

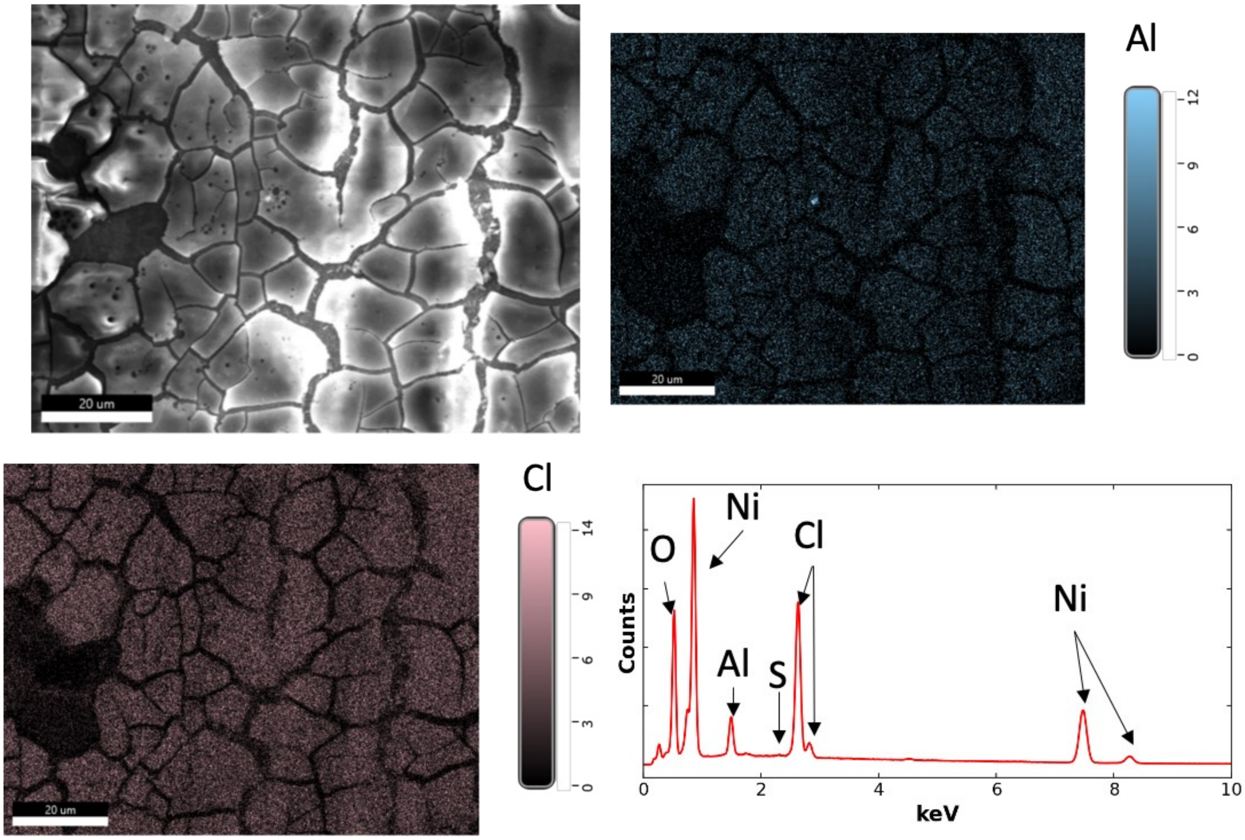

Figure S2. Scanning electron micrograph (top left) and Energy Dispersive X-Ray maps for Al (top right) and Cl (bottom left) of the Ni foil electrode after holding a 2M $AlCl_3$ electrolyte at -0.2 $mAcm^{-2}$ for 30 min. Bottom right contains an EDX spectrum from the mapped region. Evidence of deposited TFSI-substituted aluminum chloride complexes is clear from Al, Cl, and S (minor) content in the deposited material. Scale bar is 20 µm.

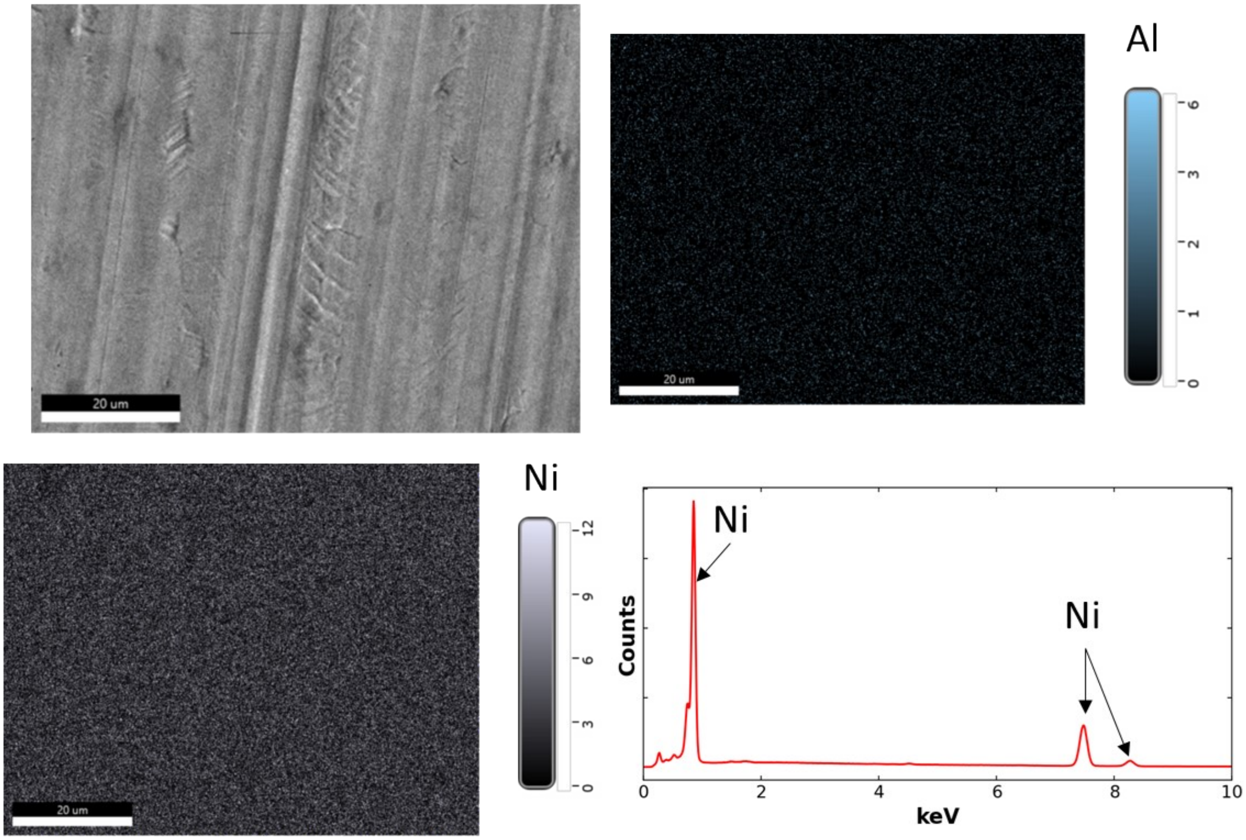

Figure S3. Scanning electron micrograph (top left) and Energy Dispersive X-Ray maps for C (top right) and Ni (bottom left) of the Ni foil electrode after holding a 2M $AlCl_3$ + 1M NaI electrolyte at -0.2 $mAcm^{-2}$ for 30 min. Bottom right contains an EDX spectrum from the mapped region. There is no significant evidence, physical or chemical, of deposited complexes. Scale bar is 20 µm.

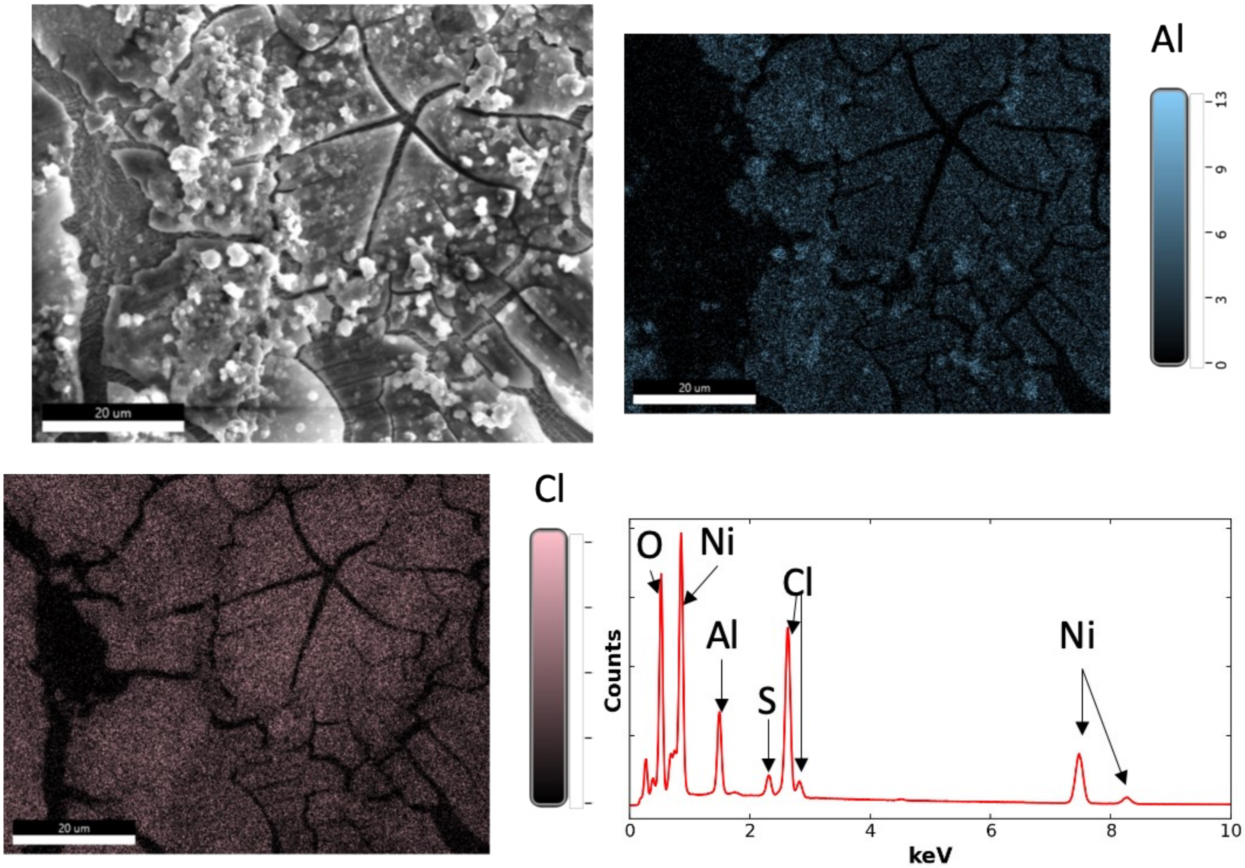

Figure S4. Scanning electron micrograph (top left) and Energy Dispersive X-Ray maps for Al (top right) and Cl (bottom left) of the Ni foil electrode after holding a 5M $AlCl_3$ electrolyte at -0.2 $mAcm^{-2}$ for 30 min. Bottom right contains an EDX spectrum from the mapped region.The most significant evidence of deposited TFSI-substituted aluminum chloride complexes is clear from Al, Cl, and S (minor) content in the deposited material. Scale bar is 20 µm.

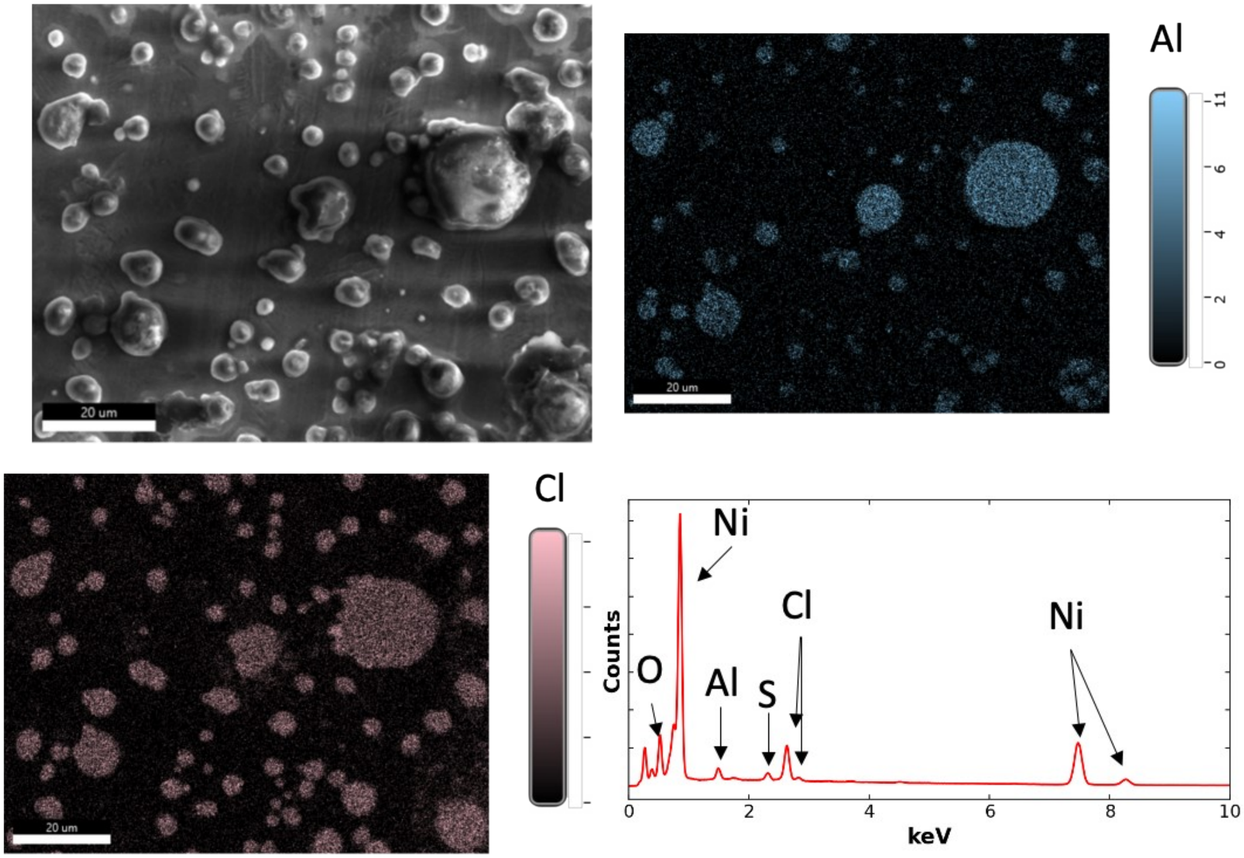

Figure S5. Scanning electron micrograph (top left) and Energy Dispersive X-Ray maps for Al (top right) and Cl (bottom left) of the Ni foil electrode after holding a 5M $AlCl_3$ +1M NaI electrolyte at -0.2 $mAcm^{-2}$ for 30 min. Bottom right contains an EDX spectrum from the mapped region. Evidence of deposited TFSI-substituted aluminum chloride complexes is clear from Al, Cl, and S (minor) content in the deposited material. Scale bar is 20 µm.

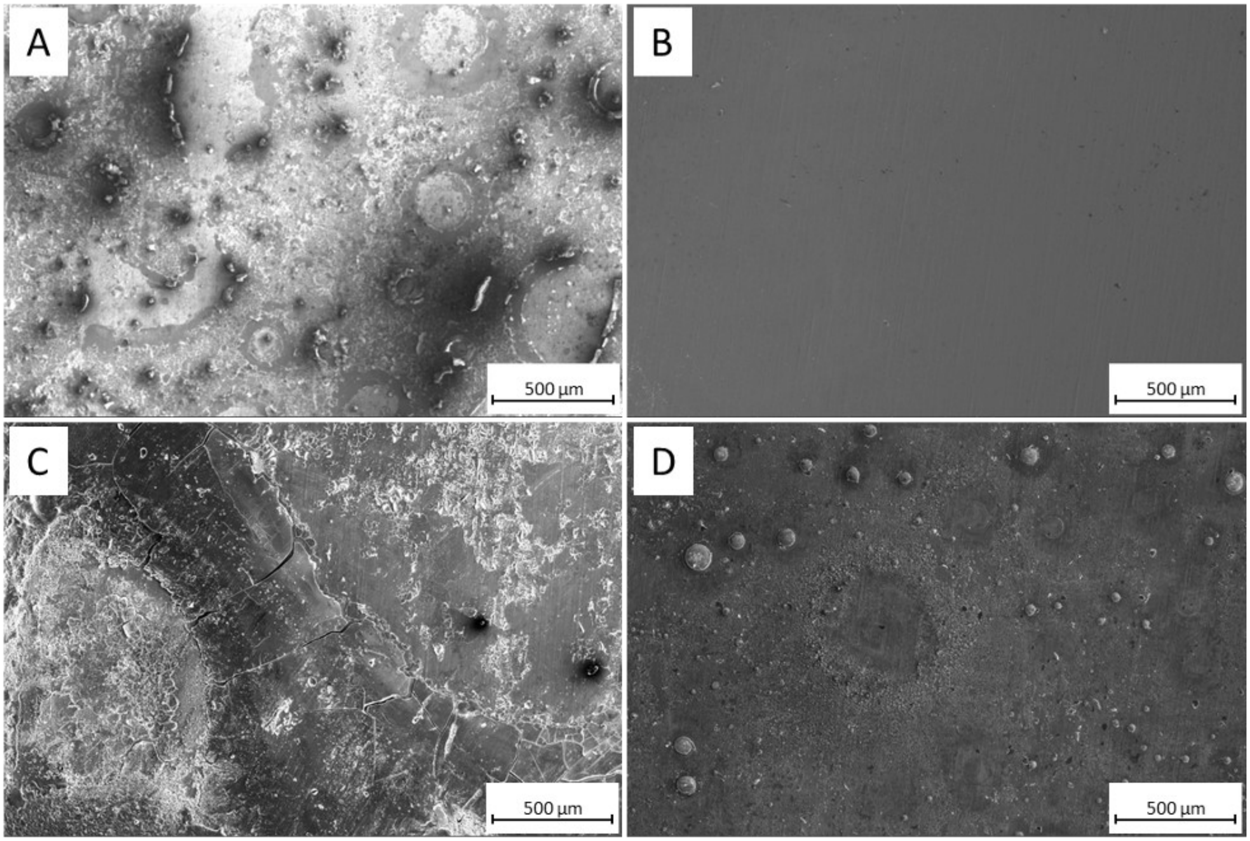

Figure S6. Lower magnification scanning electron micrographs comparing deposits on Ni surfaces after 30 min at -0.2mAcm^{-2} under in the following solutions: 2M AlCl$_3$ (A), 2M AlCl$_3$ + 1M NaI (B), 5M AlCl$_3$ (C), 5M AlCl$_3$ + 1 M NaI (D).

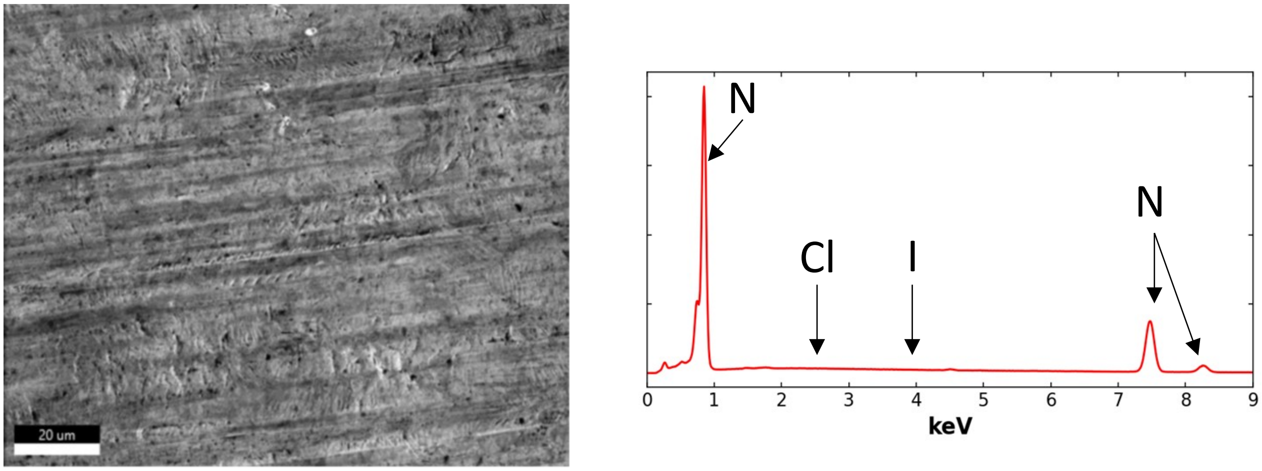

Figure S7. Scanning electron micrograph (left) and Energy Dispersive X-Ray spectrum for the Ni foil electrode after holding a 2M $AlCl_3$ electrolyte with 1M NaI at -0.2 $mAcm^{-2}$ for 30 min and +0.2 $mAcm^{-2}$ for 30 min. The absence of the element iodine at 3.937 keV or chlorine at 2.622 keV in the spectrum shows there is no oxidation of the Ni surface as this would have formed nickel halides ($NiCl_2$ or NiI_2). Scale bar is 20 µm.