

Reversible Intercalation of Bis(trifluoromethanesulfonyl)imide Anions from an Ionic Liquid Electrolyte into Graphite for High Performance Dual-Ion Cells

Ionic liquids (ILs) are promising electrolyte candidates for improving the safety of lithium ion cells. The ionic components of the IL, which is added to the lithium salt in organic solvents as electrolyte, act as charge carriers along with Li ion in the electrolyte. The movement of these charge carriers opens up a possibility of storing the charge by intercalating them in the host matrix. Researchers from the University of Münster propose a novel dual-ion cell in which both Li⁺ and the anion from the IL are used to store the charge. The study was performed on metallic Li/KS6 graphite and Li₄Ti₅O₁₂ (LTO)/KS6 cells. The formulation of 1 M LiTFSI (lithium bis(trifluoromethanesulfonyl)imide) with IL N-butyl-N-methylpyrrolidinium TFSI (Pyr₁₄TFSI) (LiTFSI:Pyr₁₄TFSI = 1:3.34) was used as an electrolyte. Depending upon the cut off-voltage and temperature, capacity exceeding 100 mAh/g can be achieved. The capacity retention of these systems remains above 90% after 500 cycles. Optimized upper cut-off voltages were determined, namely from 4.8 to 5.1 V for the metallic lithium-based system and from 3.2 to 3.6 V for the LTO-based dual-ion cell. The columbic efficiency is more than 99% despite the higher cut-off voltages. The reversible intercalation of TFSI⁻ along with Li⁺ demonstrates a novel dual-ion cell for energy storage.

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Pulse-Plating of Copper-Silver Alloys for Interconnect Applications

Continued miniaturization of microelectronics increases the detrimental impact electromigration has in copper interconnect systems. Since co-deposits with Cu hold promise for mitigating electro- and stress-migration, researchers from New York investigated the plating of Cu-Ag alloys, chosen because, for Ag addition below ~1 wt%, the resistivity can be kept below the industry target. Conventional copper plating electrolytes contain chloride and organic additives, both critical for enabling defect-free filling of surface features. The authors determined that the removal of chloride (with which Ag⁺ has low solubility) or substituting different additives (which can adversely complex either ion) could not yield deposits acceptable for this application of plating Cu-Ag alloys. Instead, the authors employed a pulse-plating scheme that permitted the additional deposition of silver via the displacement of copper atoms by silver ions during the off time of the duty cycle. These researchers demonstrated the corresponding effects Ag⁺, chloride, and additive concentrations, as well as plating conditions, had on the ultimate alloy composition and film roughness. Continuous deposits, with large grains, of an alloy having

0.3 wt% Ag were achieved in an electrolyte containing 10 ppm chloride, polyethylene glycol (PEG), bis-(3-sulfopropyl)disulfide (SPS) and polyvinylpyrrolidone (PVP) (as a leveling agent).

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Electrochemical Reduction of Carbon Dioxide Using a Copper Rubeanate Metal Organic Framework

The conversion of CO₂ into useful hydrocarbons has been of interest since the beginning of the 20th century. It remains important today, especially given the desire to efficiently utilize CO₂ (instead of releasing it into our environment) and the need to develop new, economical processes to produce liquid fuels. Among the key technical challenges is the development of catalysts with high activity for CO₂ reduction and high selectivity in the production of desirable products (including formic acid, which can be used to make methanol and other fuels). Recently, researchers at the Panasonic Corporation in Japan reported their work exploring the first ever electrochemical reduction of CO₂ at a working electrode consisting of a copper rubeanate metal organic framework (CR-MOF). The authors prepared working electrodes by dispersing the CR-MOF particles on carbon paper, and then conducted potentiostatic electrolysis experiments in a 3-electrode cell containing 0.5 M KHCO₃. They demonstrated that the CR-MOF electrode was superior to copper (known as a material capable of catalyzing the formation of hydrocarbons) in terms of product selectivity (100% formation of formic acid on CR-MOF compared to 87% on Cu) and yield (13.4 μmol/cm²/h for formic acid formation on CR-MOF vs. 1.1 μmol/cm²/h on Cu) for electrolysis experiments conducted at -1.2 V vs. SHE.

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Distinguishing Between Individual Contributions to the Via Resistance in Carbon Nanotubes-Based Interconnects

Several emerging technologies have been proposed to replace copper in future interconnect schemes, and the use of carbon nanotubes (CNT) is promising. The International Technology Roadmap for Semiconductors proposes CNT interconnects in vias, but mitigating unwanted effects from processing remains a challenge. Researchers at Chemnitz University of Technology and the Fraunhofer Institute for Electronic Nano Systems in Germany demonstrate CNT vias based on a hybrid metal/CNT technology, integrated on a Si platform using standard back-end-of-line (BEOL) processing. The team used a substrate-based selective catalytic CNT growth, keeping the CNTs localized within the vias. Through electrical testing of a statistically significant 440 individual structures, they show that the resistance of two series-connected vias is quite low after chemical mechanical

planarization of the structures. Importantly, they confirm that resistance of single CNT-containing vias is determined by the contact resistance of the CNT-metal interface, which originates from partial oxidation of that interface during processing. They propose that additional resistance can stem from stress-induced void formation in the copper (Cu) caused by the high temperatures needed to catalyze and grow the CNTs. By virtue of this investigation, a route to lowering CNT resistance when used in vias is also proposed by forming TaN barriers to prevent void formation in the Cu interconnect.

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Improvement of Mobility in ZnO Thin Film Transistor with an Oxygen-Enriched MgO Gate Dielectric

Fast and reliable alternatives to Si-based thin film transistors (TFTs) have been intensely investigated in recent years, and some oxide materials such as ZnO have shown excellent characteristics. Robust and efficient performance can depend on lowering the operating voltage, which is typically accomplished using high-κ dielectrics. Researchers from the National Cheng Kung and Far East Universities in Taiwan, have managed to improve the carrier mobility in bottom-gated, top-contacted TFTs made from ZnO using oxygen-enriched MgO dielectric layers. The team used the MgO to influence the polarity of the ZnO layer and demonstrated that the (002) face of the ZnO in contact with the (111) plane of MgO, which gives a favorable band structure for improved field-effect mobility of 78.3 cm² (Vs)⁻¹, three times better than non-enriched MgO-based ZnO TFTs. Usefully, the method also reduced grain boundary density resulting in improved charge accumulation and operation. The team shows that a TFT device can operate with significantly enhanced field-effect mobility due to oxygen-enriched MgO. The work highlights the beneficial effect of successfully balancing the oxygen deficiency in the ZnO layer with the oxygen enrichment of the MgO gate dielectric to improve the electrical properties of the physical interface and overall TFT performance.

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