Enhancement of the electrochemical performance of zinc–silver batteries with a gold nano-scaffold†

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Primary zinc–silver batteries are widely employed in military, aerospace, and marine applications. However, the development of secondary zinc–silver batteries is still a subject of on-going research. For example, these batteries suffer from rapid capacity loss during cycling due to instabilities of the zinc anode and the silver cathode. While there is a large body of work on the Zn anode, there is limited work toward stabilizing the Ag electrode and thereby achieving a long cycle life. In this work, we propose a gold–silver nanostructure where gold acts as a scaffolding material and improves the retention of structural integrity during cell cycling. We show that this nanostructure improves battery capacity as well as capacity retention after 35 cycles. Our work emphasizes the role of nanostructuring in enabling a newer secondary battery chemistry based on existing primary ones.

Introduction

Li-ion batteries are considered the go-to-chemistry for most energy storage applications. However, they are costly, environmentally unsafe and also present operational hazards.1–4 Aqueous chemistries with high energy density can be ideal candidates to overcome these limitations.5,6 Zinc–silver (Zn–Ag) batteries are one such example, where zinc and silver act as the anode and cathode, respectively.5,7,8 The reactions in the electrodes (in alkaline medium) are as follows:

Anode:

\[ \text{Zn(OH)}_2 + 2e^- = \text{Zn} + 2\text{OH}^-, \]

\[ E_{\text{Zn}^{2+}/\text{Zn}}^{\text{red}} = -1.22 \text{ V vs. SHE}, \]

Cathode:

\[ \text{Ag}_2\text{O} + \text{H}_2\text{O} + 2e^- = 2\text{Ag} + 2\text{OH}^-, \]

\[ E_{\text{Ag}^{2+}/\text{Ag}}^{\text{red}} = 1.56 \text{ V vs. Zn}^{2+}/\text{Zn}, \]

and

\[ 2\text{Ag} + \text{H}_2\text{O} + 2e^- = \text{Ag}_2\text{O} + 2\text{OH}^-, \]

\[ E_{\text{Ag}^{2+}/\text{Ag}}^{\text{red}} = 1.82 \text{ V vs. Zn}^{2+}/\text{Zn}. \]

The higher volumetric capacity of Zn (5854 mA h cm$^{-3}$) compared to Li (2062 mA h cm$^{-3}$)9 and the use of various safer aqueous electrolytes like ZnCl$_2$ (neutral or mild)10 and KOH (alkaline)7 in zinc–silver batteries make this class of batteries attractive particularly for defence, military and aerospace applications.11,12 While these afford a high energy density (300 Wh kg$^{-1}$ for Zn–Ag compared to 150 Wh kg$^{-1}$ for Li),13 so far they are restricted to being primary batteries. The various stability issues at the Zn electrode like dendritic growth formation,14 parasitic gassing,15 and electrode dissolution after multiple charge–discharge cycles10 and also the electrochemical and mechanical stability issues at the Ag electrode16 are responsible for such restriction. There is significant research work on stabilizing zinc anodes and improvement of the electrolyte, predominantly because of their utility in Zn–air batteries.10,13,16 However, challenges at the Ag electrode are rarely addressed.

Certain factors responsible for the poor performance of Ag electrodes are degradation of the separator,17 formation of resistive Ag$_2$O and migration of Ag ions.18 The conductivity of electrodes has been increased by addition of more conductive substrates like reduced graphene oxide (rGO)13 and acetylene black.19 However, these additives are associated with high contact resistance, thus adversely affecting the battery performance. In alkaline medium, the loss of Ag ions has been addressed by the use of mild/neutral electrolytes like ZnCl$_2$10 however, the working potential achieved in this medium is lower than that achieved in the alkaline medium.

Additionally, the oxygen evolution reaction (OER) has been found to decrease the cycle life. It was proposed that gold plating increases the overpotential for OER. It is necessary to minimize Ag dissolution from the electrodes to the solution,
which decreases the cyclability drastically. The way forward can be alloying Ag electrodes with other metals. As reported by Scharf et al., introduction of Au as an electroplating material improves the cyclability by almost a factor of 10 while retaining a capacity of 12.5 mA h cm$^{-2}$. The authors showed that electroplating with gold greatly improved cyclability. Thus motivated, we designed a bimetallic nanomaterial that could also address these problems.

We therefore focused on nano-structuring a Ag electrode by integrating Au into it. We hypothesize that the presence of Au increases the electrical conductivity of Ag$_2$O, as well as its structural stability through the incorporation of a nano-scaffold. Significant improvements in battery capacity retention and the working potential window were realized through optimization of the Ag electrode alone. The capacity retention of Au-incorporated Ag electrodes was determined and was shown to be far superior to the capacity retention of an Ag electrode prepared with Ag nanoparticles via aerial oxidation. For the preparation of Au-incorporated Ag$_2$O electrode $\sim$1 nm Ag nanoclusters were embedded in an Au matrix through a colloidal route. When used as an active material for Zn–Ag batteries, this showed an improved electrode performance compared to pure Ag nanostructured electrodes, in terms of capacity achieved, better capacity retention after 35 cycles and energy density achieved. We show that the incorporation of Au is responsible for improved electrode stability, thus increasing the lifetime of the electrode material and enhancing its electrochemical performance.

Results and discussion

One of the important challenges in nanoparticle synthesis is the control over size, shape, and morphology of the particles. A slight change in the crystallographic structure can change various properties like catalytic, optical, electrical, magnetic, etc. The most convenient route established so far is the colloidal route, which involves the reduction of metallic salts to pure metals in the presence of certain capping agents like surfactants, ligands or polymers. These capping agents act as templates providing a strained environment for the growth of particles and hence restricting the growth of the particles to the nano-regime and helping the particles acquire particular shapes. However, a limitation associated with this template-mediated synthesis is the loss of monodispersity of the nanoparticles arising from changes in the nano- or microstructure of the templates during the experiment. Jana et al. and Nikoobakh et al. have shown that control over the shape and size of nanoparticles can be better achieved in the case of seed-mediated synthesis of nanostructures in the presence of soft templates like cetylammmonium bromide (CTAB).

The specific problem of nanostructuring of Ag through Au incorporation also required us to address the issue of miscibility of the two metals. This is done through careful control of a wide range of parameters including temperature, pH of the medium and mechanical agitation. Although Au and Ag have similar lattice types (fcc) and lattice constants [\(\sim 4.08 \text{ Å}\)] and are soluble in each other in all proportions, past studies have nonetheless highlighted the successful retention of independent silver and gold phases in collooidally prepared nanostructures. This unique feature of colloidal synthesis enables the realization of gold–silver heterostructures. This has been explained through the quantitative estimation of the activation barriers associated with the alloying process. Due to the large activation barriers [\(\sim -1.7 \text{ eV}\)], extensive alloying is not observed in colloidal reactions conducted at temperatures below 50 °C.

We therefore restricted our reaction temperature to 25 °C. These materials were prepared in two discrete steps. First, silver nanoparticles were prepared, and subsequently silver–gold nanostructures were synthesized by co-precipitation of the Au and Ag nanoparticles from the colloidal solution (Fig. 1a, schematic).

Previous studies have shown that silver nitrate (AgNO$_3$) dispersed in any surfactant can produce silver halide particles that can act as a precursor for Ag nanoparticles. So, in a typical procedure 0.5 mL of 10 mM AgNO$_3$ (aqueous) was added to the aqueous solution of 2 mL of 0.1 M cetylammmonium bromide (CTAB), followed by addition of a reducing agent, 2 mL of 0.1 M freshly prepared, ice-cold, sodium borohydride (NaBH$_4$) solution after a certain time lag (~30 s). The reaction mixture was maintained at 25 °C at this stage. After 30 s due to the formation of silver halide precipitates, the reaction mixture appeared turbid. But the exact time taken showed a slight variation with the usage of different CTAB batches, even when constant temperatures were maintained. With the reagent batches mentioned in the ESI, we found that the addition of NaBH$_4$ 20 s after AgNO$_3$ addition led to the best results in terms of restricting Ag nanoparticles to the desired size and maximizing their stability in the colloidal solution. This method results in a dispersion of ~1 nm sized nanoparticles (Fig. 1b). The size determination in this figure was performed by first casting the colloidal solutions of nanoparticles onto a mica substrate. Subsequently the particle diameter was probed using an atomic force microscope (AFM) in tapping mode. Small silver nanoparticles such as the ones pre-

![Fig. 1](image-url) (a) Schematic of the synthesis of Ag–Au nanostructures. Prominent reagents are mentioned. (b) Size distribution of the Ag nanoparticles as measured by AFM.
pared here are known to exhibit indistinct plasmon features (see Fig. S1†) due to the large inelastic electron scattering by the particle surfaces.

Immediate addition of 1 mM chloroauric acid (HAuCl₄) to the reaction mixture produces Au nanoparticles. The amount of HAuCl₄ added was varied depending on the composition of the nanoparticles (details in the ESI†). The remaining NaBH₄ in the solution reduces the injected HAuCl₄, thus leading to the formation of an Au–Ag colloid.

The Ag–Au hybrid electrode was prepared by precipitating nanoparticles from the colloidal solution through the addition of iso-propyl alcohol (IPA) (shown in Fig. 1a). The amount of IPA added was optimized to control agglomeration to a level where the composite nanoparticles could be conveniently redispersed for the preparation of a smooth film suitable for use as a battery electrode. Typically, 3 mL of IPA was added to 5 mL of reaction volume, which led to apparent darkening of the resulting solution. The final step involved centrifugation of the dark brown reaction mixture at 4100 RCF for 5 minutes. The dark precipitate adhering to the sides of the centrifuge tubes is mainly composed of partially aggregated nanoparticles. The clear supernatant is discarded. The precipitate is dried under a vacuum of ~10 mbar. Depending on the measurements to be performed, the black precipitate was either dispersed in chloroform (CHCl₃) or 3 M aqueous potassium hydroxide (KOH) solution.

We show the structural properties of these Ag–Au nanostructures in Fig. 2. The data were collected using a Themis TITAN transmission electron microscope (TEM) at 300 kV. For this analysis, the sample was dispersed in CHCl₃ and the solution was dropcast onto a carbon-coated copper grid. Fig. 2a shows a typical transmission electron micrograph of Ag–Au nanostructures and exhibits a broad size distribution, with the particle size varying from 8 nm to 40 nm. Despite the presence of a tail of large-sized nanoparticles, the distribution has a median of 11.42 nm, with most of the particles in the range of 9–11 nm (Fig. 2b). High-resolution TEM (HRTEM) images (Fig. 2c) show the polycrystalline nature of most nanoparticles. This is consistent with the behavior expected from a random aggregate prepared by destabilizing a colloidal dispersion. The selected area electron diffraction (SAED) image of the nanoparticles is shown in Fig. 2d. The SAED pattern of the planes is consistent with fcc Au and Ag crystallographic planes. This is further confirmed from the powdered X-ray diffraction (PXRD) pattern of the bimetallic nanostructures (Fig. S2†). Fig. 2e–g show the high-angle annular dark field (HAADF) image and the elemental mapping of the nanostructures, respectively. The elemental maps further emphasize the random distribution of Au and Ag over the entire nanoparticles. On average nanoparticles are composed of a 9 : 1 molar ratio of Ag : Au.

The transmission electron micrograph of the nanoparticles shown in Fig. 2 is obtained from a small-scale synthesis. However, when the synthesis is scaled-up by a large (×10) factor, the structural properties of the nanoparticles obtained differ from those described above. Fig. 3 shows the elemental mapping of two areas of the sample obtained from large-scale synthesis. The lack of a homogeneous dispersal of Au and Ag in various parts of the material is notable. For example, Fig. 3a–c show a region with a lower-than-average percentage of Au (10%). At the same time, we observe separate Au-rich nanostructures in other regions of the sample (Fig. 3d–f). An inhomogeneous Au distribution is undesirable for the electrode. Hence, samples from multiple batches of small-scale synthesis were collected to prepare the electrode.

To prepare an electrode, the Ag–Au nanostructures collected after centrifugation were redispersed in a 3 M aqueous KOH solution. After fifteen minutes, the above alkaline solution of nanostructures was centrifuged at 9000 RCF for 5 min. The precipitate adhered to the sides of the centrifuge tube and the supernatant was colourless. After discarding the supernatant,
the precipitate was collected and dried in a vacuum (~10 mbar) overnight.

We used these bimetallic nanostructured particles to prepare the Ag electrodes as a substitute for regular Ag electrodes in a Zn–Ag battery to study the effects of this structural motif on the battery capacity and cyclability.

The electrochemistry experiments performed for this purpose involved a two-electrode set-up where a 0.5 cm × 2 cm Zn metal foil was used as the counter electrode and reference electrode. This enables any differences in observed performance to be directly attributable to the performance of Ag–Au nanostructured electrodes. For the working electrode, the active material i.e., a mixture of bimetallic nanostructure, polytetrafluoroethylene (PTFE) binder (60 wt% PTFE dispersion in H₂O, Sigma Aldrich) and Conductive Carbon Black (TIMCAL Graphite and Carbon Super P) in a weight ratio of 7 : 1 : 2, respectively, was prepared. A small amount of distilled water was added to the mixture, and it was sonicated and vortexed for an hour to make a slurry. Finally, the slurry obtained was dropcast on 1 cm × 3 cm Aecarb P-50 carbon paper. The as-prepared electrode was dried at 60 °C in a vacuum oven for 12 hours and then used as the working electrode. As the Zn–Ag battery exhibits better performance in alkaline medium, 7 O₅ M aqueous KOH solution was used as the electrolyte for all electrochemical measurements. All the experiments were carried out under an argon atmosphere and at room temperature.

The reduction processes for Zn and Ag in alkaline medium are as follows:

\[
\text{Zn(OH)}_2 + 2e^- \rightarrow \text{Zn} + 2\text{OH}^-, \\
E_{\text{Zn}^{2+}/\text{Zn}} = \text{-1.22 V vs. SHE},
\]
\[
\text{Ag}_2\text{O} + \text{H}_2\text{O} + 2e^- \rightarrow 2\text{Ag} + 2\text{OH}^-, \\
E_{\text{Ag}^{2+}/\text{Ag}} = \text{1.56 V vs. Zn}^{2+}/\text{Zn},
\]

and

\[
2\text{Ag} + \text{H}_2\text{O} + 2e^- \rightarrow 2\text{AgO} + 2\text{OH}^-, \\
E_{\text{Ag}^{2+/Ag^-}} = \text{1.82 V vs. Zn}^{2+}/\text{Zn}.
\]

Zn–Ag batteries thus exhibit two discharge voltages at 1.56 V vs. Zn²⁺/Zn and 1.82 V vs. Zn²⁺/Zn depending upon the Ag species undergoing reduction.

Cyclic voltammograms (CV) were obtained at a scan rate of 1 mV s⁻¹ for two different potential windows, 1 V to 1.9 V vs. Zn²⁺/Zn (Fig. 4a) and 1.2 V to 2 V vs. Zn²⁺/Zn (Fig. 4b) for Ag–Au nanostructures. For a smaller potential range, a single redox reaction is observed with a reduction current peak at ~1.42 V vs. Zn²⁺/Zn. However, in the wider potential window, two redox reactions at ~1.5 V vs. Zn²⁺/Zn and ~1.8 V vs. Zn²⁺/Zn have been observed. From the above values of reduction potentials (vs. Zn²⁺/Zn), it is evident that the reduction current peaks around 1.4–1.5 V and 1.8 V correspond to Ag / Ag and Ag²⁺/Ag⁻ redox, respectively, when measured with Zn metal as the reference electrode. The slight difference in the values of the reduction potential with respect to the standard values of Ag can be attributed to the presence of Au in the active material as well as crystallographic features such as stacking faults and exposed planes that are associated with the nanostructured electrode material. 9,12,43 Furthermore, in this bimetallic nanostructured electrode, Au is not participating in the redox reaction. The reduction potential of the Au⁻ / Au coulpe is 2.12 V vs. Zn²⁺/Zn, which is beyond our working potential window. Therefore, we do not observe any additional peak corresponding to the Au redox in the CV curves.

To estimate the stability of these new Ag–Au nanostructures as active Zn–Ag battery materials, galvanostatic charge–discharge (GCD) experiments were performed in two potential windows (1.4 to 1.9 V and 1.3 to 2 V vs. Zn²⁺/Zn) to probe 1 e-redox (Ag₂O → Ag) and 2 e-redox (AgO → Ag₂O → Ag) under similar conditions to those mentioned above. Fig. 4c and d show the GCD plots for 35 cycles for a potential range of 1.4 V to 1.9 V at a current density of 444 µA cm⁻² and for an extended potential range of 1.3 V to 1.97 V at a current density of 534 µA cm⁻², respectively, for Ag–Au nanostructures (Ag : Au = 90 : 10). Initial discharge capacities of 83 and 155 mA h g⁻¹ have been presented in Fig. 4e and f, respectively.

To understand the influence of Au on the electrode, the same set of experiments as mentioned above was repeated for pure Ag nanoparticles (Fig. 5a–f). It is observed that the initial discharge capacities for both the one e-redox and two e-redox of Ag–Au nanostructures (83 and 155 mA h g⁻¹) were much higher than those of Ag nanostructures (55 mA h g⁻¹, Fig. 5c and 80 mA h g⁻¹, Fig. 5d). Furthermore, we have observed the improvement in capacity retention after 35 cycles for Ag–Au nanostructures (~80% for Ag–Au vs. ~55% for Ag nanostructures). Additionally, the energy density obtained for the 1 e-redox is also higher for Ag–Au (90 : 10) (121 W h kg⁻¹) compared to pure Ag (90.5 W h kg⁻¹). This suggests that the improved performance is because of the presence of Au in the nanostructures.
Despite this advantage, the two e-redox (1.3 V to 2 V) suffer from higher capacity degradation after 35 cycles (~56% for Ag–Au and ~60% for Ag) even after the incorporation of Au in nanostructures. The higher drop in Coulombic efficiency over 35 cycles may be due to the lower conversion efficiency of Ag(n) → Ag(0) when compared to Ag(i) → Ag(0).44 Previous studies have attributed this capacity loss during cycling to the instability of the divalent silver ion in alkaline medium.45,46 The unstable nature of Ag(n) accelerates its decomposition to the Ag(i) state, which is also accompanied by oxygen evolution.45,46 Furthermore, the lower capacity retention for a wider potential window is consistent with parasitic reactions as noted in previous reports.15

The improved performance due to Au incorporation plausibly occurs because the Au matrix restricts silver agglomeration in the binary composite, while such a restriction is absent in the case of pure silver nanoparticles. Therefore Au enhances the structural stability which enhances the tolerance for Ag(II) decomposition to Ag(I).42 To further validate this hypothesis, GCD was performed for two additional compositions of 80 : 20 and 70 : 30 Ag : Au ratios in the battery electrodes. As shown in Fig. 6a, for the potential range of 1.3 V to 1.9 V vs. Zn2+/Zn (1 e-redox) the highest initial capacity (94 mA h g⁻¹) and final capacity after 35 GCD cycles (76 mA h g⁻¹) were achieved for the battery comprising an 80 : 20 Ag : Au electrode. The energy density obtained for this composition is also the highest (141 W h kg⁻¹). 80 : 20 Ag : Au electrodes also show the highest initial capacity for 2 e-redox over the potential range of 1.3 V to 2 V vs. Zn2+/Zn (Fig. 6b). The initial capacity, final capacity and energy density obtained for the 80 : 20 Ag : Au electrode are 220 mA h g⁻¹, 120 mA h g⁻¹ and 354 W h kg⁻¹, respectively. This further confirms the improved structural stability provided by the Au scaffold. However, the initial capacity achieved decreases when the amount of Au was increased to 30%. This may be due to the decrease in the electroactive material (Ag) in the nanostructure. The corresponding GCD curves are shown in Fig. S6.†

To investigate capacity degradation, electrochemical impedance spectroscopy (EIS) (Fig. 7) was performed in a 2-electrode configuration for the 80 : 20 Ag–Au electrode. The 80 : 20 Ag–Au electrode was chosen because it afforded the best initial and final capacities amongst the four compositions that were experimented with in this work. The data were collected over a frequency range of 1 Hz to 100 kHz with an AC excitation voltage of 20 mV. Experimentally obtained EIS data (black filled square in Fig. 7a) were fit (red closed circles in Fig. 7a) using a Randles circuit (inset of Fig. 7a). Based on EIS analysis, there is an increase in the constant phase element Q1 and a decrease in the charge transfer resistance, R2, with increasing cycle number. We note that a predominant contribution to Q1 will be the double layer capacitance. The increase in Q1 with increasing cycle number (Fig. 7b) is attributed to the formation of a highly resistive Ag2O precipitate caused by incomplete conversion of Ag2O to AgO on the electrode.47,48 Q1 increased from 1005 µF s⁻¹ (n = 0.65) for cycle 1 to 8353 µF s⁻¹ (-n = 0.64) for cycle 35. Furthermore, we attribute the decrease in the charge-transfer resistance (R2) to Ag dissolution during cycling. The Ag dissolution leads to an increase in the electronic conductivity and an associated decrease in the charge transfer resistance of the Ag–Au electrode. R2 decreased from 40 Ω for cycle 1 to 10.7 Ω for cycle 35.

Scanning-Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDS) was performed to assess any changes in the electrode composition before and after cycling. Based on these experiments, summarized in Table S2,† we observe a decrease in the percentage of Ag for all Ag : Au electrodes after
Therefore, we conclude that capacity fading in these electrodes is due to Ag dissolution. Nevertheless, we note that Ag dissolution is minimized in Ag: Au nanostructures when compared to electrodes with Ag nanostructures without any Au scaffolding. Our observation that loss of silver ions is majorly responsible for capacity degradation and poor cycle life in Zn–Ag/AgO batteries are consistent with previous reports.49 From the above discussion it is thus evident that a nano-structured bimetallic system is a viable substitute for Ag nanoparticle electrodes as well as conventional Ag electrodes in alkaline Zn–Ag batteries. For this material to become an alternative to pure Ag in Zn–Ag batteries, it is further necessary to verify the retention of its structural integrity after multiple cycles of electrochemical measurements. We therefore examined the electrodes before and after electrochemical measurements using HAADF-STEM (Fig. 8a–f).

From the elemental mapping (Fig. 8b and c) of the material before measurement corresponding to the HAADF image in Fig. 8a, we see that Au and Ag nanoparticles coexist in the electrode composite. The elemental mapping (Fig. 8e and f) of the area corresponding to the HAADF image in Fig. 8d after 35 charge–discharge cycles also shows a similar microscopic elemental distribution. We thus infer the resilience of bimetallic Ag–Au electrodes to structural degradation under repeated cycling. Furthermore, the structure appears to retain its initial structure after successive charge–discharge cycles and segregation of Au and Ag domains is not observed. The data in Fig. 8 highlight these observations after 35 electrochemical cycles. The robust structure of Ag–Au nanostructures makes them viable electrode materials for Zn–Ag batteries.

**Conclusion**

In conclusion, we proposed and synthesized a nanostructured material containing Au and Ag. The bimetallic Ag–Au material provides higher starting capacities, improved capacity retention after 35 GCD cycles and higher energy density. The highest initial capacity, final capacity and energy density were achieved in the case of Ag: Au (80:20). Nanostructuring proposed in this work enables us to realize a battery potential of 1.9 V vs. Zn²⁺/Zn, which is ~0.5 V higher compared to the maximum accessible in an acidic or neutral medium.7 We show that these nanostructures resist degradation into separate Ag and Au phases leading to improved structural stability of the electrode upon repeated cycling, thus explaining the improved electrode performance. Our results highlight the potential of rechargeable Zn–Ag chemistry to emerge as a viable alternative to existing rechargeable battery technologies.

**Data availability**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Author contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Conflicts of interest**

There are no conflicts of interest to declare.

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