**Impact of anode substrates on electrodeposited zinc over cycling in zinc-anode
rechargeable alkaline batteries**

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Abstract: Electrochemical behavior of Ag, Bi, Cu, Fe, Ni and Sn substrates on zinc deposition was evaluated over battery cycling by cyclic voltammetry and electrochemical impedance spectroscopy. The effect of Bi, Cu, Ni, and Sn substrates on zinc electrodeposition during battery cycling was investigated using scanning electron microscopy and X-ray diffraction. The corrosion behavior of each metal in 9 M KOH and the corrosion rates of zinc plated on each substrate were analyzed by Tafel extrapolation method from the potentiodynamic polarization curves and electrochemical impedance spectroscopy. Although the charge-transfer resistance (R_{ct}) of zinc electrodeposition is lowest on Sn, Sn eventually corrodes on cycling in alkaline media. Use of Ni as a substrate causes zinc to deteriorate on account of rapid hydrogen evolution. Bi and Cu substrates are more suitable for use as current collectors in zinc-anode alkaline

rechargeable batteries because of their low corrosion rate and compact zinc deposition over battery cycling.

Key words: Zinc; Alkaline batteries; Electrodeposition; Substrates

1 Introduction

Use of zinc as the anode for alkaline rechargeable batteries has gained attention due to zinc's low cost, high specific energy density, high equilibrium potential, ease of handling and environmental friendliness [1]. Zinc anodes are being developed for a number of commercial applications including small consumer products and large grid-scale battery backup systems [1]. To current date, commercialized technologies of zinc anodes are not capable of cycling more than 500 cycles at high depth of discharge (DOD) without deep cleaning step and more than several thousand cycles at low DOD, such as 10% [1,2]. Recently, a novel "flow assisted" zinc-nickel battery was proven to cycle its zinc anodes at ~95% DOD for 3000+ cycles in small batteries and 1000+ cycles in a large 36 kWh demonstration [3].

However, one of the main challenges that hinder the widespread use of rechargeable zinc anodes is the formation of porous or dendritic zinc during cycling, which leads to battery failure. Various approaches have been applied to avoid this problem and obtain compact zinc deposits [4–10]. Previous research has focused on the impact of current density and flow rate on the zinc morphology [11–13], additives in the electrode and electrolyte [14–17], separator improvement [18], pulse charging and electrode vibration [18].

Various metal substrates have been used to improve the efficiency of zinc deposition either by increasing the overvoltage of the parasitic hydrogen evolution reaction (HER), accelerating zinc deposition kinetics or altering the crystal habit of electrodeposited zinc [19–21]. HER gas formation has been shown to affect the zinc deposit morphology [22–24]. Morphology of zinc electrodeposition also has a preferred crystal orientation that is dependent on current density and electrolyte mass transfer properties [25]. Each plane of zinc crystal has a corresponding free energy of electrodeposition, which generates different corrosion resistance on the various crystal faces [26]. For example, the preferred orientation of zinc on brass (11 $\bar{2}$ 2) correlates with a high coulombic efficiency (95%+) during battery cycling [25]. The early stage of compact zinc electrodeposition was also studied on carbon-coated TEM grids [27], where it was demonstrated that (00 $\bar{0}$ 2) zinc single-crystals merge to form polycrystalline compact zinc thin films. It has also been reported [19] that crystallographic mismatch between the substrate and zinc deposit affects the zinc adhesion and subsequent morphology, in particular that islands of zinc form on substrates of larger crystallographic misfit. Therefore, zinc deposits are fine-grained on Cu but are large boulders on Fe and Ni. Chu *et al.* [20] and McBreen *et al.* [21] explored zinc deposition on various substrates from zincate solution, including Cu, Au, Cd, Pb, Ti, Sn and In. Pb and Cd substrates have been used commercially in rechargeable zinc electrodes since they produce adherent zinc deposits, inhibit zinc dendrite growth and suppress zinc corrosion (i.e. self-discharge). However, both Pb and Cd have environmental problems that have ended their widespread commercial use. Due to all these interactions, the choice of substrate plays a strong role in the performance,

cycle life and commercial viability of zinc anodes, especially when zinc is plated on the bare substrate at the start of each cycle.

Much of the past work that is applicable to zinc electrodeposition is unclear whether the same predictions can be extended to long-term cycling in batteries. Substrate effects were only investigated on shallow charging. Deep cycling has not been investigated previously. On extended cycling it is seen that some substrates cause zinc deposits to rapidly degrade, making it impossible to use them during the typical cycling potentials observed in alkaline zinc anodes. In this work, the aim is to investigate the effect of environmental friendly substrates on zinc cycling performance.

2 Experimental

Cyclic voltammetry, impedance measurements and corrosion studies were performed on a rotating disk electrode setup, using PTFE encased 5 mm diameter rods of Ag, Bi, Cu, Fe, Ni and Sn (99.9%+ pure) purchased from Alfa Aesar. The electrodes were successively polished with 400, 600, 1200-grit sandpaper, and then finished with 1 micron and 0.05 micron alumina polishing powder. The potential readings of all the experiments were measured against Hg|HgO reference electrode (Koslow). The electrolyte was 60 g/L ZnO (0.74 mol/L) dissolved in 37% potassium hydroxide (9 mol/L KOH). The KOH solution was freshly prepared by dissolving analytical reagent (AR)-grade KOH (Sigma-Aldrich) pellets in deionized water. In order to imitate the real battery operation, the electrolytes were not deaerated. For zinc-anode battery system, the main challenge that accompanies with zinc deposition is hydrogen formation on the anode

during charging. Hence, deaerating the electrolyte does not affect the observation significantly. A Pine Instrument MSR-type rotator at 100 rpm was used in all the experiments, except for the cyclic voltammetry experiments and studies of corrosion rate where 0 rpm was used. A Versastat 4 potentiostat (Princeton Applied Research) and an EC-potentiostat (Bio-logic Science Instruments) were used for all the electrochemical behavior experiments.

To measure the evolution of roughness and porosity (compactness) during many cycles of electrodeposited zinc, flat sheets (6.45 cm^2) of Bi, Cu, Ni and Sn were used as the anode substrates in a prismatic flow-assisted cell with a 3 mm gap between the cathode and anode. The setup of prismatic flow-assisted cell is the same as our previous studies [11,28,29]. Bi sheets were prepared by physical vapor deposition of Bi onto Cu sheets. Galvanostatic (constant current) cycling experiments were carried out using an Arbin BT2000 battery tester. The electrolyte was 0.74 M ZnO dissolved in 9 M KOH solution. The electrolyte flows from the bottom to the top of the cell at a flow velocity of 0.8 cm/s. Current densities of the galvanostatic experiments were 12.5 mA/cm^2 , 25 mA/cm^2 and 37.5 mA/cm^2 . The cross-section of zinc deposition morphology on each substrate at the specified current densities was examined in a scanning electron microscope (SEM) at charge density of 50 C/cm^2 and 100 C/cm^2 after the first and sixth charge cycles. The sample treatment procedure is described elsewhere [11]. Briefly, the samples were treated with epoxy and cured after which they were cut in three segments, and the cross section of zinc morphology of each segment was examined by a Zeiss Supra 55 VP FE-SEM. X-ray diffraction (XRD) was used to investigate the effect of substrates on the

crystallographic orientation of zinc deposition morphology during cycling. XRD experiments were carried out in a Philips Panalytical diffractometer operating at 40 kV/40 mA from 30 to 140 degree with a Cu-K α filter at a scan rate of 0.188 degree/s.

3 Results and Discussion

3.1 Electrochemical analysis

3.1.1 Cyclic voltammetry

Cyclic voltammograms of disk electrodes of our various substrates were scanned at 10 mV/s from -1.8 V to 0.2 V, as shown in Fig. 1. These data present cathodic and anodic peaks of zinc deposition and dissolution. In the cathodic direction, the onset potentials for zinc deposition on Ag, Cu and Sn are slightly higher than that on other metals, indicating that Ag, Cu and Sn are more facile for zinc to deposit on. It is observed that hydrogen bubbles evolve more readily on Ni [30,31]. Hydrogen (H₂) evolution imbalances the cathode versus anode and causes loss of coulombic and energy efficiency. Hydrogen evolution is more drastic during the first cycle relative to subsequent cycles. In table 1, typical hydrogen overvoltages at current density 1 mA/cm² on the metal substrates are reported [30,31]. The higher hydrogen overvoltage is indicative of less hydrogen evolving on the metal substrate. Fe and Ni electrodes have earlier H₂ evolution due to the low activation overpotential [30,31].

In the anodic direction, additional oxidation peaks are observed, indicating the dissolution of an alloy or oxide phase. For example on Ag substrate, in the anodic sweep

direction peak Zn_a occurs at -1.3 V due to the dissolution of metallic zinc, then other anodic peaks Ag_{al} and Ag_{aII} appear at -1.15 V vs. Hg|HgO and -0.31 V vs. Hg|HgO, respectively. Peak Ag_{al} was ascribed to ϵ -phase alloy $AgZn_3$ and peak Ag_{aII} is to ζ -phase alloy $AgZn_3$ by Hendrikx *et al.* [32]. These two alloy peaks are formed through diffusion [32]. During the cathodic sweep at 0.15 V vs. Hg|HgO peak Ag_{cl} takes place, which is ascribed to Ag reduction reaction. For Bi substrate, in the cathodic direction, Bi deposition forms the cathodic peak near -0.7 V vs. Hg|HgO then it deposits at its limiting current density from -0.8 V to -1.4 V vs. Hg|HgO [33]. During the anodic sweep Bi oxidation occurs at -0.37 V vs. Hg|HgO. During zinc deposition on Cu, a cathodic shoulder at -1.1 V is seen, which was attributed to underpotential deposition of zinc [34]. By comparison, Sn does not show underpotential deposition or alloys with zinc. The current–voltage relationship for a Sn electrode in 9 M KOH and 0.74 M ZnO solution shows that during the cathodic scan an anodic peak Sn_{cl} rises around -0.92 V vs. Hg|HgO, which likely exists due to destruction of a passivation layer that was previously prohibiting the electrochemical dissolution of tin. Peak Sn_{cII} is where Sn reduction reaction happens [35]:

The anodic peak Sn_{al} and the shoulder Sn_{aII} are due to electro-dissolution and formation of a passivation layer respectively. A precipitation of SnO or $Sn(OH)_2$ is formed at the electrode surface, which corresponds to peak Sn_{al} [36].

Zinc dissolution is most pronounced on Sn substrate, followed by Fe, Ag, Ni, Bi and Cu. While Bi has similar electrochemical properties as Pb, it is much less toxic and stable in alkaline media. Fe and Ni are not recommended because of their tendency toward hydrogen evolution, although several previous papers successfully use nickel substrates at high coulombic efficiency for thousands of cycles [3]. Based on the cyclic voltammetry data, Ag, Bi, Cu and Sn are the most promising anode substrates of this group for zinc rechargeable alkaline batteries.

Table 1 Typical hydrogen overpotentials for current density of 1 mA/cm² on some metals [30,31]

Metal	Ag	Bi	Cu	Fe	Ni	Sn
Overpotential η/V	0.475	0.78	0.45	0.4	0.3	0.75

3.1.2 Electrochemical Impedance Spectroscopy and corrosion tests

Cyclic electrochemical Impedance Spectroscopy (EIS) experiments were carried out to compare the charge transfer resistance R_{ct} of the bare substrates over 50 cycles of zinc deposition and dissolution. The applied EIS potential amplitude was 5 mV placed on top of a steady -1.45 V to maintain the zinc deposition process. The EIS frequency range was 100 KHz to 10 Hz. For each of the 50 cycles, zinc was deposited on each substrate for 1 C (5 C/cm²) at -1.45 V then depleted galvanostatically at 25 mA/cm² until the potential dropped to -1.1 V. EIS measurements were collected after each deplating was completed. Charge transfer resistance at the end of each cycle was determined from the impedance plot. In Fig. 2a, Bi is found to have high R_{ct} at the first few cycles but it improves over cycling. Slow kinetics at the first few cycles was probably due to the formation of Bi

layer prior to zinc deposition. Sn has the lowest R_{ct} , and R_{ct} is stable on Ag over cycling. The increase of R_{ct} on Cu gradually during cycling may result from the depleting of zinc underpotential deposition. Fe anode fails on account of rapid hydrogen evolution and Ni anode deteriorates due to high charge transfer resistance R_{ct} . R_{ct} of substrates over zinc deposition/dissolution increases in the order: Sn<Bi<Ag<Cu<Ni<Fe over battery cycling. The corrosion current densities (i_{corr}) of the different substrates in 9 M KOH solution were measured by potentiodynamic polarization technique. This method may only approximate and provide an upper bound on the corrosion rate, and cannot distinguish between dissolution of metal or formation of surface oxide films, but it is still helpful for comparison on the relative electrochemical activity of the different substrates. The potential scan ($v=0.166$ mV/s) was performed without stirring the solution, starting from a potential 250 mV more cathodic than the corrosion potential and then followed by scanning in the anodic direction towards 250 mV more anodic than the corrosion potential. Each experiment was performed at least three times. The Tafel polarization curves were obtained and shown in Fig. 2b. The corrosion current densities (i_{corr}) were obtained from the Tafel plots by extrapolating the linear portion of the curve to the corrosion potential. Table 2 shows the results of the corrosion parameters for each substrate in 9 M KOH solution based on this method. The estimated upper bound on corrosion rates decrease in the order: Sn>Bi>Cu>Ag>Ni>Fe. However, Ni and Fe have comparable values.

Table 2 Parameters for the corrosion of metal substrates in 9 M KOH solution

Substrates	$E_{\text{corr.}}/\text{mV vs. Hg HgO}$	$i_{\text{corr.}} \mu\text{A}/\text{cm}^2$	$\beta_a \text{ mV}$	$\beta_c \text{ mV}$
Ag	150.022	8.499	104.1	121.8
Bi	-571.879	46.219	18.7	98.4
Cu	-492.317	17.973	41	58.1
Fe	-982.018	1.224	74.9	54.1
Ni	-213.645	1.612	103.7	86.6
Sn	-1099.671	93.908	30.1	273.9

Additional EIS measurements were collected to compare the charge transfer resistance R_{ct} of zinc deposits covering the different substrates, before and after a 12-hour rest in the electrolyte. During EIS measurements the substrate was held at an applied potential amplitude of 5 mV placed on top of a steady voltage which is equal to OCV. The frequency range was 100 KHz to 10 Hz. Before collecting the EIS measurements, zinc was deposited on each metal substrate for 10 C ($50 \text{ C}/\text{cm}^2$) at $25 \text{ mA}/\text{cm}^2$. Figs. 2c and 2d compare the Nyquist plots of zinc deposition on different substrates before and after a rest in KOH for 12 hours. Fig. 2e shows the equivalent electrical circuit used for the EIS plots. Charge transfer resistances were calculated based on the equivalent circuit and are shown in table 3. It indicates that after zinc deposits on different anode substrates, the corrosion rates of zinc decrease in order: $\text{Fe} > \text{Ni} > \text{Sn} > \text{Cu} > \text{Bi} > \text{Ag}$. Also, after the cells rest for 12 hours, the corrosion rates of zinc deposition decrease in order: $\text{Ni} > \text{Fe} > \text{Cu} > \text{Sn} > \text{Bi} > \text{Ag}$. Since zinc deposited on nickel dissolves back to solution within the 12-hour rest, it demonstrates that zinc on Ni is more corrosive. It also has good agreement well with the result from the OCV measurement shown in Fig. 3.

Table 3 Charge transfer resistance R_{ct} of zinc deposition on different anode substrates

Substrate	R_{ct} /ohms	
	No rest	12 hours rest
Ag	35.94	15.06
Bi	22.19	12.13
Cu	6.33	3.10
Fe	1.93	2.15
Ni	2.15	—
Sn	4.20	5.56

The zinc was deposited galvanostatically on Ag, Bi, Cu, Ni and Sn in 9 M KOH with 0.74 M ZnO solution with a geometric area of 0.2 cm² for charge density 50 C/cm² at 25 mA/cm² then were left for rest at OCV for 12 hours then deplated. Electro-dissolution proceeded under 25 mA/cm² until the voltage reached -1.3 V vs. Hg|HgO. Fig. 3 demonstrates the self-discharge of zinc deposited on the various substrates. It indicates that zinc deposition could maintain the expected potential on Ag, Bi, Cu, Fe and Sn. Corrosion of zinc was provoked on Ni substrate. To compare the corrosion of zinc deposition on substrates, same tests were also conducted on substrates except for resting zinc deposition for 12 hours. Table 4 demonstrates even though Fe maintains the expected potential, zinc corrodes drastically on Fe. The results from table 4 indicate that corrosion of zinc on Fe and Ni are pronounced, while it is comparable on Bi, Cu and Sn. Ag substrate is the least for zinc to corrode.

Table 4 Corrosion of zinc deposition on substrates during OCV

	Coulombic efficiency % (No OCV rest)	Coulombic efficiency % (12 hours OCV rest)	Amount of zinc corrodes at OCV (%)
Ag	100	90.1	9.9
Bi	99.6	76.8	22.8
Cu	100	76.6	23.4
Fe	96.2	13.8	82.4
Ni	90.7	—	90.7
Sn	99.5	77.5	22

3.2 Substrates performance on battery cycling

3.2.1 Coulombic efficiency measurements

The substrate metal has a strong effect on the performance of zinc anodes, especially at the earliest stage of zinc electrodeposition due to their diverse H_2 evolution rate and impact on the crystal orientation of zinc deposition. Rotating disk electrodes (RDE) were used to investigate the performance of Ag, Bi, Cu, Fe, Ni and Sn substrates on zinc plating and deplating. The amount of charge passed in all the experiments was 5 C/cm^2 . Fig 4a shows the performance of the metal substrates tested on the first cycle at different current densities. Rotation speed of RDE was set at 100 rpm for each experiment, corresponding to a mass-transfer limiting current density of 55 mA/cm^2 , and the chosen current densities were fractions of this limiting current density. Electro-dissolution proceeded until the voltage reached -1.3 V vs. Hg|HgO . Fig. 4a indicates that Sn has the

best performance amongst these anode substrates at various current densities. Other anode substrates demonstrate better performance on zinc deposition/dissolution efficiency at current density ratio of 0.4-0.45.

In Fig. 4b, zinc deposition was cycled where each cycle was defined by deposition at -20 mA/cm^2 until 5 C/cm^2 were passed and then dissolution at 25 mA/cm^2 until the voltage reached -1.3 V . The results indicate that Fe and Ni do not have desirable performance due to hydrogen evolution, which is hypothesized due to HER gas becoming trapped on the downward-facing rotating electrode surface. These results agree with the cyclic voltammogram experiments. The hydrogen evolution on Fe and Ni was visible with the naked eyes. Ni and Fe anodes failed within 50 cycles. The coulombic efficiencies were 95%+ for Ag, Bi, Cu and Sn substrates. However, as we stated before, we note that 3000+ cycles are achievable in different flow and cycling conditions when Ni is applied as the substrate [3].

3.2.2 Gas measurements

Hydrogen evolution as a parasitic reaction happening together with zinc deposition leads to decrease of energy efficiency. The anode substrate plays an important role in this reaction. Hydrogen generation rates on Ag, Bi, Cu, Fe, Ni and Sn were tested in a fully sealed prismatic cell with an upside down graduated cylinder [37]. It is a typical method of measuring gas generation. The volume of water pushed out from the graduated cylinder corresponds to the volume of hydrogen generated on charging. Since the batteries were not operated under the potential region where oxygen generation happens;

hence, the gas that was being collected was mainly hydrogen. In this way, the rate of hydrogen evolution is determined. A sintered Ni(OH)_2 cathode was used, with a capacity of 0.18 Ah. The electrodes were 1 in^2 and the electrolyte was 9 M KOH mixed with 0.74 M ZnO. The amount of coulombs charged in the cell during charging was 50 C/cm^2 . The charging current density is 25 mA/cm^2 and the discharge current density is (calculated from Ni cathode capacity which is might not be relevant) 28 mA/cm^2 . The gas generated during cycling displaces the water out from the cylindrical tube. The volume of excluded water during a certain time is the way of expressing gas generation rate (Table 5). Less gas is generated on Ag, Bi and Cu. Gas evolves drastically on Ni. Fe generates less gas than Ni but hosts high HER compared to other substrates. Initially, Sn does not initiate gas formation; however, with increasing cycle life, it becomes highly active for HER, and this is likely because Sn degrades in alkaline solution. As a result, zinc corrodes quickly on Sn during battery cycling. Hydrogen generation occurs not only as a competitive reaction during zinc deposition but also occurs during OCV and discharging as a pair reaction of zinc corrosion. Ag, Bi, Cu and Sn are suitable as anode substrates in zinc-anode rechargeable batteries to suppress hydrogen evolution.

Table 5 Gas generation rate (μL/min) on anode metals

	1 st charge	5 th charge	10 th charge
Ag	2.15	1.67	1.45
Bi	2.03	3.78	3.95
Cu	3.15	3.38	2.87
Fe	2.79	4.15	4.12
Ni	11.13	13.42	14.25
Sn	2.54	4.23	4.57

3.3 Zinc deposition characterization

3.3.1 Surface roughness of zinc deposition on different anode substrates

A prismatic flow-assisted cell was used to study the evolution of roughness and porosity of zinc electrodeposition on Bi, Cu, Ni and Sn. The limiting current density of plane electrodes in the walls of a flow channel is also given by equation

$$i_{\text{lim}} = \frac{nFDC_0}{d_e} Sh$$

$$Sh = 1.85 Re^{1/3} Sc^{1/3} (d_e / L)^{1/3}$$

where i_{lim} is the limiting current density, n is the number of electrons in the reaction, F is Faraday's constant, D is the diffusion coefficient, which is reported as $8 \times 10^{-6} \text{ cm}^2/\text{s}$ [38], C_0 is the bulk zinc concentration, Sh is Sherwood number, Re is Reynolds number, Sc is

Schmidt number, d_e is the hydraulic diameter and L is the plate length in the streamwise direction. According to the equation, the limiting current density of this configuration was -55 mA/cm^2 and it was also confirmed by linear potential sweep technique, which is a way to measure the mass transfer limiting current density.

The zinc morphologies were correlated to the ratio of current density to limiting current density (i/i_{lim}). In addition, the minimum of total cell resistance R_{tot} is reported to occur around $i/i_{\text{lim}}=0.5$ [25]. The current densities of our experiments were 12.5 mA/cm^2 , 25 mA/cm^2 and 37.5 mA/cm^2 , which correspond to i/i_{lim} of 0.23, 0.45 and 0.68, respectively. Fig. 5 shows the cross-sectioned images of zinc deposition on Bi, Cu, Ni and Sn at the first and the sixth cycles separately. In these images the zinc deposits appear as darker grey and the metal substrates as the brightest grey. Compact zinc appeared lighter grey, and porous branched mossy zinc appeared darker. Figs. 6a and 6b show the compact layer thickness of zinc deposition formed on Bi, Cu, Ni and Sn at the first and the sixth cycles when charge densities 50 C/cm^2 and 100 C/cm^2 were put in. Sn forms the thickest compact layer of zinc. Cu and Bi have similar compact zinc morphology. Figs. 6c and 6d demonstrate the overall porosities of zinc deposition on metal anodes. The porosities of zinc electrodeposition were calculated based on the cross-sectioned SEM images by using Image J software. Zinc deposition formed on Ni has the highest porosity due to hydrogen formation. The order of porosities of zinc deposition on each metal is $\text{Ni} > \text{Bi} > \text{Cu} > \text{Sn}$. However, with cycling the porosities of zinc deposition on Bi and Cu are close to each other, and also, Sn has the least tendency for zinc to form high porous morphology. The zinc deposition on Ni is highly porous. The high porosity of zinc

deposition makes electron transfer difficult, which is due to the low local current density, zinc deposition occurs close to OCV, and has a higher kinetic resistance.

Fig. 7 shows the surface morphology of zinc deposition on Ni, Cu, Bi and Sn. More closely stacked zinc has higher coulombic efficiency and high corrosion resistance. Deposition of zinc on Sn has layer-like structure. Zinc deposition on Bi and Sn is in the form of stacked plates. More compact deposition was found when Bi, Cu and Sn were used as substrates compared to Ni. As a result of hydrogen formation, porous zinc generates more easily on Ni substrate that was also shown in the X-ray spectrum afterwards.

3.3.2 XRD and preferred orientation results

The crystal texture of zinc deposition has been related to zinc corrosion [39–43]. X-ray diffraction was applied to study the texture feature of zinc deposition formed on Bi, Cu, Ni and Sn sheets with 1 in² surface area. XRD patterns of zinc deposition on different anode substrates at different charge density and different cycle numbers in Fig. 8 demonstrate the evolution of texture feature of zinc morphology.

The preferred orientation was reported in terms of a texture coefficient (TC). Preferred orientation of electrodeposited zinc was quantified and the textured coefficients [44] of each reflection face were calculated as following:

$$TC = \frac{\frac{I_{hkl}}{I_{hkl}^0}}{\left(\frac{1}{n}\right) \sum \left(\frac{I_{hkl}}{I_{hkl}^0}\right)}$$

where I_{hkl} and I_{hkl}^0 are the crystal face (hkl) diffraction integral intensity of the deposit and the standard sample respectively; n is the number of the reflection faces in diffraction spectroscopy. TC values of each sample were reported in table 6 and table 7. A value of $TC > 1$ demonstrates preferred orientation of the plane is present in the sample.

Table 6 TC values of each orientation of zinc deposition on different substrates at 25 mA/cm²

		(002)	(100)	(101)	(102)	(103)	(110)	(112)
1 st Charge	Ni	0.981	0.994	0.761	1.268	1.425	1.519	2.414
	Cu	0.451	1.439	0.281	1.632	2.124	1.595	2.502
	Bi	1.754	0.787	0.231	2.369	—	5.319	2.482
	Sn	0.875	1.089	0.562	3.407	—	1.743	4.359
6 th Charge	Ni	0.814	0.972	0.678	1.616	1.021	1.804	3.127
	Cu	0.737	1.337	0.732	1.256	1.563	1.606	1.893
	Bi	0.817	1.339	0.405	2.276	2.945	2.709	2.632
	Sn	0.882	0.921	0.895	1.645	1.443	0.875	1.248

Table 7 TC values of each orientation of zinc deposition on different substrates at 37.5 mA/cm²

		(002)	(100)	(101)	(102)	(103)	(110)	(112)
	Ni	0.449	0.433	0.453	1.458	—	9.485	3.213
1 st	Cu	1.959	—	0.522	2.214	2.543	—	2.877
Charge	Bi	0.982	0.401	0.611	2.413	—	3.964	2.999
	Sn	—	—	0.442	5.851	—	—	10.345
	Ni	0.931	0.971	0.937	1.227	—	1.571	1.638
6 th	Cu	—	0.539	1.053	—	—	3.643	3.834
Charge	Bi	0.839	0.971	1.053	1.279	—	1.136	1.646
	Sn	0.909	1.057	0.906	1.439	1.473	1.295	1.935

The texture of zinc depositions demonstrated that (002) basal plane has the highest corrosion resistance. Pangarov [45] stated that (100) crystal plane is dominant under intermediate current density. It has been found that texture of zinc deposition on different substrates varies. At 25 mA/cm², high angle prismatic (100) orientation was inhibited when zinc was deposited on Bi or Sn, i.e. high energy and lower packing density. When using Sn substrate, low energy basal plane (002) was suppressed and high angle pyramidal (112) orientation was provoked. Low energy high atomic packing plane (002) was increased when Bi and Cu were being used as substrates. Low angle pyramidal orientation (103) was increased on Bi substrate. Since Bi substrate was prepared by physical vapor depositing Bi on Cu, there were some planes corresponding to Cu peaks as well. On Ni substrate, zinc crystal structure matches the pure zinc powder diffraction

that has no texture. The absence of texture on Ni substrate corresponds to mossy zinc morphology. When zinc was cycled for the 6th time, low energy high packing density basal plane (002) and prismatic plane (100) were promoted on Bi and Cu. Pyramidal plane (112) was inhibited on Cu. The texture of zinc deposition has good agreement with zinc morphology. Zinc deposition on Bi and Sn contains more basal planes and pyramidal planes that have higher corrosion resistance.

4 Conclusion

The effects of Ag, Bi, Cu, Fe, Ni and Sn substrates on electrodeposited zinc were studied by using cyclic voltammetry technique, electrochemical impedance spectroscopy, and linear polarization method. Bi was found to have higher R_{ct} at the beginning but it improves with time. Sn has the lowest R_{ct} , while the R_{ct} is stable on Ag over cycling. Cu has low R_{ct} at the beginning however it increases with cycling. Ni anodes deteriorate on account of rapid hydrogen evolution. Corrosion rates of metal anodes in 9 M KOH solution decrease in the order: Sn>Bi>Cu>Ag>Ni>Fe. Although Sn has the highest coulombic efficiency, it degrades over cycling. The porosity of zinc deposition on metal anodes decrease in the order: Ni>Bi>Cu>Sn. Considering price of metals and performance of metal substrates in zinc-anode rechargeable flow batteries, Bi and Cu are the best choices for zinc anode substrate.

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Figures

Figure 1 Cyclic voltammograms of zinc reaction on Ag, Bi, Cu, Fe, Ni and Sn rotating disk electrodes (100 rpm) at scan rate of 10 mV/s. Scan range is from -1.8 V to 0.2 V vs. Hg|HgO

Figure 2 (a) Effect of cycle number on R_{ct} at the start of zinc deposition on metal Ag, Bi, Cu, Fe, Ni and Sn substrates (charge density=5 C/cm² and $i=25$ mA/cm²) (b) Polarization curves of substrates Ag, Bi, Cu, Fe, Ni and Sn in 9 M KOH ($v=0.166$ mV/s) (c) Nyquist plots of a zinc layer on different substrates before and (d) after 12 hours rest where the inset plots are a zoomed view. No Ni data is available after 12 hours because the zinc dissolved completely. (e) Equivalent electrical circuit of the electrochemical impedance spectroscopy from Figs. 2c-2d

Figure 3 Self-discharge of zinc deposition on metal anodes where the inset plots are a zoomed view (After depositing zinc for 50 C/cm² under 25 mA/cm² then anodes were left at OCV for 12 hours). The metal substrates were rotating disk electrodes. On Ni electrode, Zn corrodes the fastest.

Figure 4 (a) Coulombic efficiency of zinc deposited on Ag, Bi, Cu, Fe, Ni and Sn at different current densities (charge density=5 C/cm²) (b) Coulombic efficiency of zinc deposited on Ag, Bi, Cu, Fe, Ni and Sn as a function of cycle number (charge density=5 C/cm² and current density i on charge=-20 mA/cm² and current density i on discharge=25 mA/cm²) The metal substrates were RDE

Figure 5 (a) Cross section images of zinc electrodeposition on metal substrates at the first cycle at 25 mA/cm² (b) at the sixth cycle (Charge density=50 C/cm²) Electrode size: 1 in²

Figure 6 (a) Compact layer thickness of zinc plated on metal anodes at the 1st cycle and (b) 6th cycle (c) Overall porosity of zinc deposition on metal anodes at the 1st cycle and (d) 6th cycle (Charge density=50 C/cm^2 & 100 C/cm^2) Electrode size: 1 in^2

Figure 7 Surface morphology of zinc deposition on Ni, Cu, Bi and Sn at $i=37.5 \text{ mA/cm}^2$

(a) Charge density= 50 C/cm^2 and (b) 100 C/cm^2 (Electrode size: 1 in^2)

Figure 8 XRD of zinc deposition under 25 mA/cm^2 at (a) cycle 1 and (b) cycle 6
XRD of zinc deposition under 37.5 mA/cm^2 at (c) cycle 1 and (d) cycle 6 (charge density:
 50 C/cm^2) Electrode size: 1 in^2